HEAT OF SOLUTION OF DILUTE SIMPLE METALLIC ALLOYS : A DENSITY FUNCTIONAL APPROACH

A Thesis Submitted
In Partial Fulfilment of the Requirements
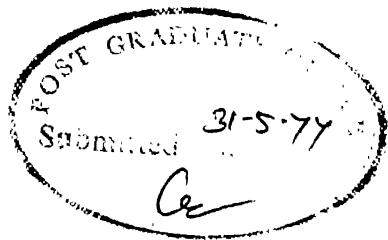for the Degree of
DOCTOR OF PHILOSOPHY

by
SUBRATA RAY

08887

to the

DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
MAY 1977

ME -1977-D -RAY - HEA

CERTIFICATE

Certified that this work 'HEAT OF SOLUTION OF DILUTE SIMPLE METALLIC ALLOYS : A DENSITY FUNCTIONAL APPROACH' by Mr. Subrata Ray has been carried out under our supervision and that this has not been submitted elsewhere for a degree.

(K.P. SINGH)
Department of Metallurgy
I.I.T. Kanpur

(T.V. RAMAKRISHNAN)
Department of Physics
I.I.T. Kanpur.

ACKNOWLEDGEMENT

Behind every study there stands a myriad of people whose help and contribution makes it successful. Since such a list will be prohibitively long I may be excused for important omissions.

The guidance, help and co-operation of Dr. T.V. Ramakrishnan is gratefully acknowledged. My association with him far excels the scope of this study and indeed it has been a great experience. His patient care made it possible for me, a hard core metallurgist to conduct this investigation. At times I could afford to falter for I knew that he was around to help me out and he did it. It is embarrasingly impossible to list out what all I got from him. So, I make no effort to do it.

Dr. K.P. Singh has always taken an extremely keen interest in this investigation. His conviction about the necessity of such theoretical studies by metallurgists made him to stand in its defence whenever it was found necessary. His understanding helped me to get over the moments of frustation and crisis generally inevitable during any research work. I thank him for his help and co-operation and also for his correct attitude reflecting his foresight.

In the end I thank Mr. C.M. Abraham for typing the thesis and Mr. Gangaram for duplicating it.

TABLE OF CONTENTS

CHAPTER 4   PARAMETRIC VARIATIONAL RESULTS AND DISCUSSION

CHAPTER 5   KOHN-SHAM METHOD IN METALS AND ALLOYS

CHAPTER 6   CONCLUSION

BIBLIOGRAPHY

APPENDIX   Gradient expansion in the density functional
approach to an inhomogeneous electron system

LIST OF TABLES

LIST OF FIGURES

S Y N O P S I S

HEAT OF SOLUTION OF DILUTE SIMPLE METALLIC ALLOYS :
A DENSITY FUNCTIONAL APPROACH
A Thesis submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY
by
SUBRATA RAY
to the
DEPARTMENT OF METALLURGY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
May, 1977

We describe in this thesis an attempt to calculate ground

state properties of dilute simple metallic alloys. The

properties of interest are the ground state energy or the

heat of solution, the equilibrium volume or density, the

electron density distribution and charge transfer. These

properties are of considerable fundamental and technological

interest. Most of the recent theoretical work in alloys is

concerned with the nature of electronic states (localized or

itinerant) and their organization in energy (i.e. density of

states). The methods developed (e.g. CPA, cluster expansion)

are not suitable for calculating the properties mentioned

first above. We apply here the general theory of the inho-

mogeneous electron gas developed by Kohn and co-workers.

In this theory, the ground state energy is shown to be a

unique functional of the electron density, being a minimum

for the correct density. The theory has earlier been applied
successfully to calculate work function and surface energy
of metallic surfaces where the electron density falls to zero
typically in an atomic distance. In case of the alloy, the
electron density changes involved are smaller. We calculate
the ground state properties of an alloy in two ways. In the
first, the electron density is parametrized suitably, and the
ground state parameters are determined variationally, by
minimizing the ground state energy. In the second, a
Schrodinger like equation derived from the variational prin-
ciple is solved to obtain wave functions $\psi_i(\vec{r})$ and the
electron density $n(\vec{r})$. The basic physical idea behind both
these methods is that of neutral, weakly coupled pseudo-atoms;
a metal atom A dissolved in B carries with it, to a good
approximation, its own electronic environment. Some density
adjustment occurs at the A-B interface.

In the first chapter of the thesis, we place in perspe-
ctive the problem of calculating the heat of solution of
alloys by summarizing the earlier largely qualitative ideas
of size effect, electronegativity, etc. due to Hume-Rothory,
Pauling and others. The application of pseudopotential
perturbation theory is also reviewed. We then describe the

inhomogeneous electron gas (density functional) theory of Kohn, Hohenberg and Sham, and outline the two major ways in which it can be applied to calculate the ground state energy of an inhomogeneous system consisting of an atom or ion A replacing the ion B in a lattice of B ions (the alloy is A_c, B_{1-c} with $c <<. 1$) (Chapter 2).

In the third chapter, we detail the variational method of finding the ground state energy (g.s.e.). The g.s.e. is assumed to be a functional of the electron density. All the terms contributing to the g.s.e., namely kinetic energy, exchange, electron correlation, electrostatic interaction and electron ion interaction are included. The approximations made are the following. 1) A local functional form is assumed for the first three terms. The forms and parameters are taken from the well developed theory of the interacting electron gas. 2) A term proportional to the square of the gradient of electron density is included. The coefficient of this term has been obtained recently in fairly sophisticated approximation schemes by various authors and by us. 3) A local pseudopotential approximates the effect of the ion on conduction electrons. We show how, given a density $n(r)$, the energy can be expressed in a rapidly convergent form. The most important term involves an

electrically neutral neighbourhood of the ion A. Because of charge neutrality, other terms, which can be calculated, are small. We discuss how the heat of solution, lattice constant, bulk modulus etc. can be calculated. In a local theory with gradient terms the only two centre dependent term in energy arises from the electrostatic interaction. Since the inter-atomic terms contribute only about 10 percent of the local, density or volume dependent terms in simple metals, our approach of concentrating on the latter is clearly reasona-ble. A more satisfactory and complete formalism is developed in Chapter 5.

In this chapter (Chapter 3) the heat of solution has been calculated with two specific variational choices of $n(r)$. Firstly, we work with one step model where the step location and height are variational parameters. One of these is fixed by charge neutrality, and we obtain analytical expressions for the heat of solution as a function of the single free parameter. The model is unrealistic in that because of the density discontinuity, the gradient term (approximation (2) of paragraph above) gives an infinite contribution. However, comparisons with a more realistic model shows that the step model gives the correct trend and order of magnitude of $\Delta \bar{H}$. In a second choice, we use a

smooth (tangent hyperbolic) distribution for $n(\vec{r})$. This leads to a two free parameter model from which heat of solution can be numerically obtained by minimization.

The systematics of the heats of solution (partial molal enthalpy at infinite dilution) is discussed in Chapter 4, for various atomic volumes and valence ratios of A and B (solute and solvent). Ignoring the small interatomic term, we find that the heats of solution show well defined dependences on size difference and on the electronegativity difference(which is defined here precisely in a new way). The numbers obtained are of the right size. We also calculate the charge transfer and attempt to make contact with various empirical and semi-empirical descriptions of alloying parameters. In a number of situations, the two parameter model does not work very well. The underlying physical causes are identified.

In Chapter 5, we discuss the Kohn Sham Schrodinger equation scheme for calculating $n(\vec{r})$ and the g.s.e. For pure metals, the scheme has been developed in a neutral pseudo-atom approximation model by Dagens, Ball and others. We present here a version of the neutral pseudo-atom model which is free from any arbitrariness, which clearly indicates the approximations involved, and allows the corrections to

be evaluated. The method is then applied to an $A_c B_{1-c}$ alloy, and the g.s.e. can be interpreted as the sum of the energy of pseudo-atom A in the B matrix, the energies of the B pseudo-atoms, and an interaction term. Preliminary results of ground state energy for pure Al, pure Mg and Al-Mg alloy are presented.

Chapter 1

Introduction

The role of electronic contribution to the free energy of
alloys was recognised from the early experiments of Hume-
Rothery and co-workers[1]. His observation led to an empirical
understanding of alloys in terms of size-difference, valency
and electron per atom ratio. These famous rules based on size-
factor, relative valence and the observation of specific
crystal structures at definite electron concentration per atom
are reviewed in the first section of this chapter in the
light of their subsequent developments. This section also
contains a discussion on the electro-chemical effect in
alloys starting from the Pauling's[2] rule for estimating the
heat of mixing from the difference in electronegativities of
the components. This rule although originally proposed for
the ionic compounds, found a successful application in alloys.
An account of the recent attempt by Hodges and Stott[3] to put
this rule for the alloys on a theoretical perspective has been
presented. This section, in essence, will tie in those as-
pects of alloys which have developed mainly from the experimen-
tal studies.

The attempt to develop a theory of alloys from the first
principles started from an urge to explain the striking

observations of the early experiments of Hume-Rothery and others leading to Jones's[4] rigid band model described briefly in Section 2. The shape of the observed fermi-surface lead one to question the correctness of the rigid band model and refinements have been proposed since. In the fifties, Friedel[5] discussed the problem of dilute alloys i.e. a single impurity in a metal, in terms of its electronic structure, polarization due to screening, scattering phase shifts and virtual bound states (See also Mott[4]). An account of the essential conclusions of these investigations is presented in Section 3.

From here the development of the theory of alloys has taken two distinctly different paths. The first one starts from a simplified hypothetical model of disorder and studies the band structure, the density of states etc. of alloys with the help of approximations known as coherent potential approximation (CPA) or the average t-matrix approximation (ATA) etc. These treatments although quite rigorous, ·. have not yet been able to estimate such useful properties as the heat of solution, charge transfer etc. We have completely left out this approach in this review. In the second approach the ground state energy (g.s.e.), known to be a unique functional of the electron density is directly evaluated. The evaluation uses the minimal property of the g.s.e. for the

correct density. Details of the electronic structure are not
obtained in this scheme; but it is specially suited for study-
ing the g.s.e. (and hence the heat of solution), charge density
and hence the charge transfer etc. It has been used successfully
for metallic surfaces by Lang and Kohn[6] and others. In the
limiting case of small periodic variation of charge density
this approach coincides with the perturbation theoretic treat-
ment of alloys formulated by Inglesfield[7] and others which
has been presented in Section 4.

1.1 Factors Affecting the Alloys :

The factors controlling the properties, of a given alloy
like the heat of solution, crystal structure etc. can be broadly
classified into two sets : (a) the environmental factor, tem-
perature and pressure which are associated with the entropy
term and (b) geometrical and electrochemical factors whose
origin are the electronic states in the alloys. The factors in
the first category have been studied thoroughly within the
framework of thermodynamics and we exclude them from our
study by considering the alloy system at $T = 0^{\circ}K$.

The second set of factors, electronic in origin, are at
issue in this study and so in this section we will take them up
for a review. The last factor mentioned in this section namely
the density mismatch effect, is not physical in origin but
is an artifact of the theoretical construction of alloy. But

since a discussion on it is relevent to this study we have presented it as a separate factor.

The factors discussed here are products of experimental studies and so have been presented in different ways by different investigators. We will discuss them broadly under two categories - the size factor and the electrochemical factor.

1.1.1 Size factor effect :

Hume-Rothery[1] was the first to realise the effect of size difference on alloying which he expressed in his famous rule 'where the atomic diameter of the solvent and solute differ by more than about 14 to 15 percent of the solvent, the size factor is unfavourable and the solid solution is very restricted. Atomic diameter is given by closest distance of approach of the atoms in the crystal structure of elements'.

This rule was arrived at while determining the limits of solid solubility of the elements of the B-subgroup with copper and silver. It was also observed that the lattice distortion produced by an increasing size factor favours a less regular structure and so the liquidus and the solidus are depressed by the size factor effect.

This rule, although negative in character, has been immensely successful in guiding metallurgists to search for systems with limited solubility where precipitation hardening can be

taken advantage for strength ning. In the last fifty years this rule has not undergone any significant change. Subsequent investigators have mainly concentrated on the definition of atomic diameter and a more reliable value for the limit in an empirical way.

The theoretical estimate of the contribution of size difference to the free energy of alloys use the approximation of an elastic continuum to represent the solvent and then considers the mechanical strain energy when the solute is inserted in this continuum. The model used is one in which a sphere of specified radius is forced into a hole of smaller or larger radius, the surfaces welded together, and the body allowed to relax in its self-stressed state. Each solute atom is thus regarded as a centre of elastic deformation.

This approach has met with a limited success in predicting solubility limits in several systems but has failed in most of the cases. The reason is not difficult to understand in view of the continuum assumption which breaks down on an atomic scale. Its success can also easily be understood if we expand the change of energy due to size mismatch, in terms of a Taylor series involving powers of the difference in size. It clearly tells us that if the size mismatch is small this approach may work.

Anoth r conceptual contradiction we encounter with the continuum model is the long range nature of strain. But if one considers from the first principles as it will be evident from our study that all the terms involved in this estimate are only short range.

Recently Hodges and Stott[3] have put forward a qualitative picture of size factor effect as distinct from electrochemical effect which the experimentalists have now way to separate. In this study we have developed the idea quantitatively within the limited framework of step model to be discussed in Chapter 2. Miedema and co-workers[8] in their empirical estimate of heat of solution in alloys have accountedfor size factor contribution to energy by a term which we fail to understand. In their first paper they assume that this contribution is proportional to the square ofdifference in electron density (Δn) of the constituents but in their subsequent papers they use a term proportional to (Δn) 2/3 without any further justification. The method of computation of Δn has also defeated us because it finally leads to $\Delta n = [(\frac{\partial^2 E}{\partial V^2})^{\frac{1}{2}}_{at\ A} - (\frac{\partial^2 E}{\partial V^2})^{\frac{1}{2}}_{at\ B}]$.

In an attempt to understand the size factor contribution, we consider the neutral atoms as separately compressible entities in alloy. This can also be justified in view of Dagen's[9] finding that interaction energy between neutral pseudoatoms is less than four percent of the energy of the

pseudoatom for alkali metals. So for the dilute alloy case where the cell size of alloy is equal to that of the solvent B we can write

$$\Delta E_{S.F.} = \frac{1}{2}(R_A - R_B)^2 \frac{\partial^2 E(r)}{\partial r^2} \quad \gamma = R_B \tag{1}$$

where R_A and R_B are solute and solvent atomic radii respectively and E is the energy of solute A with atomic radius r and $\frac{\partial^2 E}{\partial r^2}$ is related to the bulk modulus of the solute A. The validity of this simple expression has been examined in the more rigorous models under study.

1.1.2 The electrochemical effect :

In contrast to the previous factor this effect has been subject to more widespread investigation. Hume-Rothery[1] in his famous rules only observed the obvious fact that with the increase of the electronegativity difference there will be an increasing tendency towards formation of compounds thereby restricting the solid solubility. The concept of electronegativity i.e. the power of an atom in a molecule to attract electrons to itself has been a guide to understand chemical reactions but the precise meaning of this power in terms of first principles is still missing. In an attempt to give a consistent empirical scale of electronegativity Pauling[2] in 1932 correlated the difference in heat of formation of ionic compounds with the square of the difference in electronegativity

of the constituent atoms. This when applied to the heat of
solution of alloys, was found to be quitesuccessful indica-
ting the importance of electro-chemical effect in alloys.
Since then several attempts have been made to understand the
concept of electronegativity and identify it with some
directly measurable property but each of them has met only
with limited success. Miedema and co-workers[8] have identi-
fied it with the work function and have tried to estimate the
electrochemical effect in alloys. But Hodges and Stott[3] on
the basis of density functional formalism and some crude
approximations have found the leading term in the express
expression for the heat of solution to be proportional to the
square of difference in the internal chemical potential of
the constituents and hence identified the electronegativity
with the chemical potential.

If $n_g(r)$ is the ground state electron distribution in
alloys then the chemical potential of the system is given by
μ as follows[6].

$$\mu = \frac{\partial E_g(n)}{\partial n_g(\vec{r})} \qquad (2)$$

where E_g is the ground state energy of the system.

In equilibrium it is the same through out the system and so
should be independent of r. Hodges and Stott[3] assume that in
the alloy A-B, atoms A and B are 'prepared' (by appropriate

compression or dilation (from their equilibrium size in the pure state) so as to 'fit' the alloy unit cell. Suppose the charge distribution now is $n_t(\vec{r})$. The electronic distribution will relax to the ground state distribution $n_g(\vec{r})$. From functional Taylor series expansion it can be shown that, upto second order

$$E[n_t] - E_g \simeq \tfrac{1}{2}\iint d\vec{r}\, d\vec{r}'\{\frac{\partial^2 E[n]}{\partial n(\vec{r})\, \partial n(\vec{r})}\}_{n=n_g} [n_t(\vec{r}) - n_g(\vec{r})]$$

$$[n_t(\vec{r}') - n_g(\vec{r}')] \qquad (3)$$

Taking derivative with respect to $n_t(r)$

$$\mu_t \simeq \mu + \int d\vec{r}\,\{\frac{\partial^2 E[n]}{\partial n(\vec{r}')\, \partial n(\vec{r})}\}_{n=n_g} [n_t(\vec{r}') - n_g(\vec{r}')] \qquad (4)$$

Substituting eqn. (3) in (2) we get

$$E[n_t] - E_g \simeq \tfrac{1}{2}\int [\mu_t(r) - \mu]\,[n_t(\vec{r}) - n_g(\vec{r})]d\vec{r} \qquad (5)$$

Now since the trial distribution corresponds to density of electron in the solute cell A after the size difference has been compensated by an increase in energy and n_B in solvent cell B then $E[n_t] - E_g$ corresponds to the negative of electrochemical contribution to the heat of solution because the change from n_t to n_g will correspond a charge redistribution for equalising the chemical potential throughout the system leading to a charge transfer giving rise to a dipole layer in the boundary of the cell A. The charge transfer Q can be estimated as

$$Q = \int_{cell \ A} [n_g(\vec{r}) - n_t(\vec{r})]d\vec{r} = - \int_{cell \ B} [n_g(\vec{r}) - n_t(\vec{r})]d\vec{r} \quad (6)$$

So, eqn. (5) can be rewritten as

$$E_g - E[n_t] \simeq -\tfrac{1}{2} Q(\mu_A - \mu_B) \quad (7)$$

Since Q can be shown to be proportional to $(\mu_A - \mu_B)$ so the attractive electrochemical contribution to the heat of solution is given by

$$\Delta E_{e.c} = E_g - E[n_t] \ \alpha \ - (\mu_A - \mu_B)^2 \quad (8)$$

Identifying Pauling's rule for heat of solution with eqn. (8) one can arrive at μ as a measure of electronegativity. In principle μ can be calculated from a knowledge of $E_g[n(\vec{r})]$. While calculating μ_A and μ_B Hodges Stott[2] took a uniform density model of pure components and were unable to get rid of r-dependence of μ. So they averaged this $\mu_A(r)$ over A cell to get μ_A. This is arbitrary and so in our study we have taken μ_A as the value of $\mu_A(r)$ at the boundary of the uniform distribution where the phenomenon of charge transfer takes place. The expression of eqn. (8) also has been examined in this study to judge the validity of Taylorseries expansion upto 2nd order used in arriving at it.

Miedema and co-workers[8], in theirestimate of this contribution are consistent with Pauling's rule but surprisingly they have identified electronegativity with the work function.

In view of the result of Hodges and Stott[3] this again is surprising because work function is the sum of the internal chemical potential μ and the potential due to the metal surface dipole layer[6]. So, unless it is shown that this potential due to the dipole layer is proportional to the internal chemical potential their measure of electronegativity is inconsistent with that of Hodges and Stott[3].

In 1966 Hume Rothery[10] revisited this area and came out with some more interesting details: (1). A tendency was observed for atoms of elements near the ends of the short periods and B-subgroups to complete their octet of electrons, and a similar but less marked tendency to fill the d-shell in the later transition metals (2) Atoms giving rise to almost pure p-bonding may not enter structures involving other type of bonds. A high value of difference in electronegativity may overcome this restriction. The last observation cannot be commented upon in this study because of difference in the approach.

1.1.3 Density Mismatch effect :

This factor is an artifact of the theoretical investigations of alloys by Hodges and Stott[3]. When the uniform density of electrons in solute cell A (n_A) and that in solvent cell B (n_B) readjusts in such a way that there is no further

charge transfer, at the boundary between these two cells a density step exists. This, due to the gradient term in kinetic, exchange and correlation energy, will give rise to an unphysical singularity in energy. So these authors have taken a small localized density component (n_c) of exponential nature over and above the uniformdistribution from both sides of this discontinuity. From the expression of chemical potential, with the help of poisson's equation $\angle$. they find out the exponents of n_c and estimate the energy change due to this n_c.

This procedure is suspect atleast on two grounds (1) The component n_c is notdetermined variationally from the minimal property of the ground state energy (2) The reference state of no charge transfer with a step in uniform distribution is misleading because these authors get this state with an averaged chemical potential where its r-variation is smeared out. This may prove unreliable in defining a no charge transfer state.

In this study we have not been able to separate this term in the strict sense. The comparison of the step model and the continuous model gives a rough idea only because in all the cases we found that the continuous models arrive at a minimum energy configuration by not only relaxing the step of the step model but producing a shift of the step also. Again the value of the slope of the density distribution ($\sim$ .7 to 3) is small indicating a significant charge transfer and consequently an

increase in the dipole energy.

1.2   Rigid Band Model

It assumes that the energy surfaces and the density of states curve of the solvent metal remain unchanged on alloying, the only effect of the addition of the solute metal being, if its valency is greater than that of solvent, to add electrons to the solvent band resulting in swelling of the Fermi-surface (F.S.) and filling the density of states curve to higher energy.

By assuming the F.S. of noble metals nearly spherical this theory provided an explanation for Hume-Rothery[10] observation of the solubility limit for f.c.c. α-phase at electron atom ratio of 1.36 in the Cu-Zn system which coincided with the peak of the density of states due to F.S. touching the zone boundary. Similar explanations were provided for the fixed electron-atom ratio for the limit of β and γ-phases in these alloys. But Pippard's experimental observation negated this explanation by showing that F.S. has already crossed the 1st B.Z. after filling it up. In an attempt to revive this explanation Hume-Rothery and Roafe[11] suggested that the limit of α-phase boundary is associated with the second peak of density of states where F.S. is making contact with the square faces of the zone. The defenders of this explanation have further pointed out

inconsistency of Pippard's result with the electronic specific heat data which was interpreted again in terms of the rigid band model. There has been attempts by several investigators to clarify the situation from different points of view[12] with limited success but still it remains an unsolved problem in alloy theory.

In this investigation none of the above mentioned aspects of rigid band model will be examined. This brief note originates for the sake of completeness only. One other experiment need be mentioned in this context - that of soft x-ray spectra in Mg-Al alloy by G.A. Rooke[13]. The spectra of Mg and Al atoms in the alloy showed different band widths very similar to pure Mg and pure Al. This stands in glaring contrast to the assumptions of this simple rigid band approach.

1.3 Friedel's Model[5]

In a solid solution the perturbing potential V_p produced in a gas of valence electrons by the solute atom is determined in this model by solving Poisson's eqn. in the Thomas-Fermi approximation.

$$V_p = \frac{\Delta Z}{r} e^{-qr} \tag{9}$$

where $q^2 = 4\pi N_0 (E_F)$ and $N_0(E_F)$ is the density of states at the Fermi energy E_F. ΔZ is the valency difference between the solute and the solvent, and r is the distance from the

solute. This expression of V_p shows polarisation of the electron gas to screen the solute potential making it localized. Since the solvent away from the solute atom is unaffected, the Fermi level E_F remains the same unless the impurity concentration is so high as to cause mutual interaction. The change in the density of states due to polarisation has been studied in great detail[5].

The rigid band relation is found to be valid when V_p is spherically symmetric provided it varies little within the wave length of the electrons with respect to the energy $E-V_p$. This is true when $E-V_p$ is not too near to the limit of the band. This approximation is also quite good at large r.

It was also shown that for strong localized perturbation bound states may occur between the energy bands and are subtracted from these bands. As these bound states are formed energy levels move out of the bottom of the conduction band with the topof the band moving down towards the Fermi level.

Inspite of this detailed study of the perturbed electron states and their polarisation,the absolute value of the heat of solution for dilute alloys could not be found out within this scheme. As a result this study finds little use in this investigation apartfrom one vital conclusion of Friedel[5] to suggest that the wave functions will always try to adjust themselves in the alloy such that the solute atoms

are very much like those in pure solute metal. Heine and Weaire[14] look at it as the quantum analog of the classical theorem that the energy density of black body radiation per unit frequency range per unit volume is independent of the boundary conditions like size, shape or nature of the container. This is in complete consonance with the results of soft x-ray spectra of Mg-Al alloys of Rooke[13] as pointed out in the last section and it forms the starting concept of the approach taken in this investigation i.e. the solute atom goes in the alloy as a piece of metal of pure solute.

1.4 Pseudopotential Perturbation Theory

Since atoms as they exist in pure metal is a very relevant concept in alloy so we start with a discussion on how the pure metal is viewed in this formalism. The density of electrons in a pure metal is conceived to consist of an uniform electron gas with a weak periodic component superimposed on it due to the perturbation produced by the pseudopotential of the ions embedded in this uniform electron gas. The energy of the uniform electron gas under pseudopotential is the structure independent term and accounts for almost ninety percent of the cohesive energy in many systems indicating that the structure dependent term resulting from periodic component is quite weak to be justifiably treated by perturbation theory. But we find that the metals with

higher valency and lower core radius (or ionic radius) the structure dependent term increases multifold in this linear response formalism. Dagens, Rasolt and Taylor[15] have calculated the charge densities and the interatomic potentials for Li^+_-, K^+_-, Mg^{++}, Al^{+++} and Ca^{++} ions embedded in uniform electron gas of corresponding metallic density self-consistently and found that the non-linear contributions are quite important. These authors tried to simulate this contribution within the framework of linear response theory by adjusting parameters of model potential but failed. Yet the success of this formalism in the calculation of different properties of pure metals stands out as a clear justification of its applicability. But in the study of the vacnacy or alloying in metals the perturbation may be quite strong even resulting in the formation of quasi-bound state and hence the second order perturbation theory may not provide a satisfactory framework for the study of the alloys.

The alloy is conceived as independent atomic cells of solute and solvent   _ uniform electron gas of corresponding metallic densities. These cells are coupled by periodic electron densities of the alloy duly modified by the presence of solute and distinct in that respect from that of solvent. The picture of coupling becomes physically transparent if represented in terms of interatomic potentials.

Here we present a brief account of this formalism following Inglesfield[7,14] mainly.

1.4.1 Alloy potential :

If, C, concentration of the solute with pseudopotential v_A and (1-C) concentration of B, the solvent with pseudopotential v_B is made into an alloy then the potential of the alloy system can be written as

$$V(r) = \sum_{i(A)} v_A(r-R_i) + \sum_{i(B)} v_B(r-R_i) \qquad (10)$$

where r is the space co-ordinate and R_i represents the co-ordinate of the ions. i(A) indicates the sites occupied by solute A atoms and i(B) are those of solvent B atoms. Taking Fourier transform of V(r) we get

$$V_{ion}(q) = \frac{1}{N} \sum_{i(A)} e^{-iq.R_i} v_A(q) + \frac{1}{N} \sum_{i(B)} e^{-iq.R_i} v_B(q)$$

$$= S(q) \bar{v} + [C S_B - (1-C)S_A] (v_B(q) - v_A(q)] \qquad (11)$$

where $S(q) = \frac{1}{N} \sum_{i} e^{-iq.R_i}$ is the structure factor and

$$S_A(q) = \frac{1}{N} \sum_{i(A)} e^{-iq.R_i} \quad \text{and} \quad S_B(q) = \frac{1}{N} \sum_{i(B)} e^{-iq.R_i}$$

$$(12)$$

are the partial structure factors. The potential is now written in terms of a mean potential $\bar{v} = C v_A + (1 - C) v_B$ and an alloying potential $v_\Delta = v_A - v_B$. Hence the alloy can be seen as a periodic array of mean potential in the

uniform electron gas intermixed with a scattering alloying potential.

1.4.2 Total energy :

The energy of the uniform electron gas or the structure independent energy per atom of alloy is given by

$$v = C \, U_A + U_B \, (1 - C) \qquad (13)$$

where U_A and U_B are respectively the energy of the uniform electron gas of densities corresponding to pure A and pure B respectively.

Now the band structure energy per atom of alloy evaluated by second order perturbation theory is given by

$$U_{BS} = \sum_q \frac{|V(q)|^2}{|k|^2 - |k+q|^2} \qquad (14)$$

where $V(q) = V_{ion}(q)/\varepsilon(q)$

gives the screened potential with $\varepsilon(q)$ as the dielectric function. To get correct value of U_{BS} we have to subtract the electrostatic self energy of the electrons which have been counted twice in the above expression and finally we get

$$U_{BS} = \sum_q V(q)^2 \, \varepsilon(q) \, \chi(q) \qquad (15)$$

where

where $\chi(q) = \frac{1}{N} \sum_{k < k_F} \left[\frac{|k|^2}{2} - \frac{|k+q|^2}{2} \right]^{-1}$

Now using expression (11) in eqn. (15) and writting the different terms in terms of their Fourier transforms we get the total band structure energy as

$$U_{BS} = \frac{1}{2N} \sum_{i \neq j} \phi_M(R_{ij}) + C^2 \sum_{i \neq j}^{(AA)} \phi_a(R_{ij}) + (1-C)^2 \sum_{i \neq j}^{(BB)} \phi_a(R_{ij}) - 2C(1-C) \sum_{i \neq j}^{(AB)} \phi_a(R_{ij})$$

(16)

where $\phi_M(R) = \frac{(Z_A + Z_B)^2}{4R} + \frac{\Omega}{4\pi^3} \int [v(q)^2 \varepsilon(q) x(q)] e^{iq \cdot R} d^3q$ (17)

is the mean atomic potential and

$$\phi_a(R) = \frac{(Z_A - Z_B)^2}{4R} + \frac{\Omega}{4\pi^3} \int [v_\Delta(q)^2 \varepsilon(q) x(q)] e^{iq \cdot R} d^3q$$

(18)

is the alloying atomic potential. Z_A and Z_B are valencies of A and B respectively.

There will be an additional electrostatic term for assuming spherical cells in place of Wigner-Seitz polyhedra U_E per atom of the alloy

$$U_E = C \, \alpha_A \frac{Z_A^2}{R_A} + (1-C)\alpha_B \frac{Z_B^2}{R_B}$$

(19)

where R_A and R_B are atomic radii of A and B respectively.

These α_A and α_B depends on the structure of A and B and is of the order of .004. Now the total energy is given by

$$E = U + U_{BS} + U_E$$

(20)

and the heat of solution per atom of   alloy   at $0^{\circ}K$ is
obtained by subtracting the energy of respective amounts of pure
A and B alloyed and it can be expressed as

$$\Delta H = \Delta U + \Delta U_{BS} + \Delta U_E$$

where, $\Delta U = U - CU_A - (1-C)U_B$

$$\Delta U_{BS} = U_{BS} - CU_{BS}^A - (1-C)U_{BS}^B$$

$$\Delta U_E = U_E - CU_E^A - (1-C)U_E^B \tag{21}$$

Apparently ΔU and ΔU_E become zero. But if we write U
and U_E not in terms of pure metal atomic radii but in terms
of alloy atomic radii then these terms are nonvanishing. All
the three terms of eqn. (20) can be written as a function of
alloy r_s, i.e. the radius of the volume occupied by an electron,
then ΔH can be variationally determined with respect to r_s.
From this r_s, alloy lattice parameters can be determined to
check Vegard's law.

1.4.3 Interatomic potential :

In Section 1.3.2, eqn. (16) we have expressed the band
structure contribution to the energy of the alloy in terms
of interatomic potential. So it is in order to write a
short note on it mentioning the uncertainties and limitations
involved.

The second term in eqn. (16) involves an integration in the reciprocal space with the dielectric function appearing along with other terms in the integrand. Johnson[16] reported that with Harrison local pseudo potential[17] for Aluminium he failed to produce any minimum in the interatomic potential, in the vicinity of the first nearest neighbor by using Hartree dielectric function Harrison[18] confirmed this and contends that the minimum appears if the non-local full pseudo-potential is used. Ashcroft[19] claimed that the interatomic potentials are quite sensitive to uncertainties in exchange and correlation and to dielectric function ε in the region $2\,k_F \leq k \leq$ few k_F. It is possible in some instances to eliminate the principal minimum in interatomic potential by ignoring exchange and correlation. The effect of density dependence of the dielectric function does have a substantial effect on the interatomic potential. The calculation of Dagens et al[15] shows marked effect of nonlinearity of the response function in the first nearest neighbor region.

From the above it can be clearly inferred that these calculations are extremely sensitive and so their reliability and consistency cannot be commented upon unless a clear understanding evolves regarding the factors involved.

1. 4.4 Choice of model pseudopotential :

In the calculation of interatomic potential in alloys
the choice of the model pseudopotentials for the constituents
is the starting point. From the scattering approach this
model potential can be viewed as one which simulates the
scattering of the band electrons correctly and hence it is non-
unique. These models, in general, contains free parameters
to be adjusted by comparing with some observed properties. The
Abarenkov, Animalu and Heine (AAH) model is fitted with the
spectroscopically observed atomic energies whereas the
Ashcroft empty core model is fitted with the resistivity data
or the lattice parameter data. These are the two models of
relevance to this study and so we briefly describe them.

From Herring's OPW method of band structure calculation one
can write

$$v(OPW) = v_{real}(r) + \sum_{c} (E-E_c) \, \psi_c(r) \, \psi_c^*(r') \tag{22}$$

where c indicates summation over the core states with the
energies E_c and the wave functions ψ_c. This equation means
that orthogenality of the valence states to the core states
can be taken care of by an equivalent transformation of the
potential as expressed in eqn. (22).

Since $v_{real}(r)$ is negative and E_c's are negative, the two terms of eqn.(22) have opposite sign and cancel to an extent inside a radius where $\psi_c(r) \, \psi_c(r)$ is substantial. This radius is called the core radius inside which the core-electrons are confined. The second term of this eqn.(22) is nonlocal in nature and if we write it in the form

$$v(r) = f(r) + \sum_l f_l(r) \, P_l \qquad (23)$$

where P_l is the projection operator separating out the corresponding l-component from the wave function. From the identity $\sum_l P_l = 1$ we write

$$0 = f_{av} - f_{av} \sum_l P_l \qquad (24)$$

Adding eqns. (23) and (24) we get,

$$v(r) = [f(r) + f_{av}] + \sum_l (f_l(r) - f_{av}) \, P_l \qquad (25)$$

If f_{av} is large and positive like the f_l then both the Brackeeted terms become small. So even if the cancellation within the core is incomplete from eqn. (22) a shift of origin by proper choice of f_{av} may make the non-local term in the potential negligible in most of the cases for simple metals. From this justification Ashcroft proposed a local empty core model for pseudo-potential of the form

$$v(r) = 0 \quad \text{for} \quad r < r_c$$
$$\quad = -Z/r \text{ for } \quad r > r_c \tag{26}$$

Here r_c is the parameter to be fitted with an observable property of the system under consideration. In our study we have used this model for our parametric variational calculation of the heat of solution of the alloy. In our pseudo atom calculation reported in the last chapter. We have used (for reasons stated there) a restricted form of AAH-potential optimised by shaw[14] to make it smoother in real space and cut-off faster in reciprocal space. This is originally a non-local potential but we have used a local form by taking only the $l = 0$ component. So, the form becomes

$$v(r) = -A_0 \text{ for } \quad r < r_c$$
$$\quad = -Z/r \text{ for } r > r_c \tag{27}$$

Shaw[14] has proposed a value of A_0 equal to $-Z/r_c$ which again makes it one parameter potential if higher l non-local contributions are neglected. It is eqn. (27) along with $A_0 = -Z/r_c$ which we have used in the last part of our study.

Chapter 2

Density functional Method in an Alloy

This method expresses the ground state energy of a many electron system as a functional of its correct charge density. This charge density in turn can be found out by using the minimal property of the ground state energy and the functional relation. The formalism is exact in principle although it involves some approximations due to our lack of knowledge of the exact functional relation for the kinetic, exchange and the correlation energy. This chapter first describes this formalism and then the approximations normally used.

Then we show how the density functional formalism can be cast as a neutral pseudoatom theory. This has been done by Dagens[9] for the pure metal case starting with some arbitrary parameters. We use two types of formulations (i) Parametric variational where the charge density is parametrised and the parameters are evaluated by minimising the energy, i.e. to get the ground state energy. This scheme is described in detail in the next chapter. (ii) The Kohn-Sham formulation where we get Schrodinger like pseudo one electron equation from the variational principle. This scheme will be dealt with a view to apply it to pure metals and alloys in Chapter 5. Here we deal with the basic formalism in brief and discuss how it is applied to the case of alloys in general.

The idea of applying this method to alloy came from its successful application to the problem of metal surface where the situation is quite similar. In the metal surface the electron density changes from that of the bulk to zero over the surface layer whereas in the alloy it changes roughly from the bulk value of the solute to that of the solvent over a similar distance. For the metal surface both the parametric variational method (in which calculations were carried through first by Smith[20]) and the Kohn Sham method (worked out by Lang and Kohn[6]) give good results for the surface energy, work function etc. We thus expect, a forteriori, that the methods should be quantitatively successful for the alloy problem also.

2.1 Density Functional Formalism

In this section we will review the general aspects of this formalism leaving out the particular application to metals and alloys which forms the bulk of this study.

Hohenberg and Kohn[21] (HK) proved a remarkable theorem which states that the ground state wave function of a many particle system, if non-degenerate, is a unique functional of the particle density. This theorem implies the existence of a universal ground state energy functional of the external potential and particle density. The energy

functional is minimum for the true particle density, so that the true ground state energy and particle density may be determined by application of a variational principle involving the particle density alone. The original proof was for a local potential and was extended for non-local potentials by Gilbert[22].

In order to apply the theorem, one must be able to construct the universal functional. It is accurately known for the limiting case of a uniform high density electron gas[23]. An approximate functional form for slowly varying electron gas[21,23] is known even for metallic densities[24]. But serious questions have been raised regarding the validity of the inhomogeneous term in view of the fact that the density gradient expansion near a nucleus where the density gradient is very high, can be shown to be divergent series and so need be summed to infinite order[25]. Local spin density theories based on HK theorem have been applied to atoms[26] and molecules[27] inspite of these troublesome questions with surprisingly good results for many applications. In all real molecules and solids the external potential results from one or more nuclii which produces a very inhomogeneous electron density distribution. But in solids if one is interested in problem concerning the valence electrons which have a more

nearly uniform density, especially if one uses a pseudo-potential to smooth out the density in the core region, this formalism provides a tool of enormous strength. Our application lies in this domain.

2.1.1 HK Theorem :

Let us consider an electron gas under the influence of an external potential $v(\vec{r})$ and the mutual coulomb repulsion. The Hamiltonian has the form

$$H = T + V + U \tag{1}$$

where (in atomic units)

$$T = \frac{1}{2} \int \vec{\nabla} \psi^*(\vec{r}) \vec{\nabla} \psi(\vec{r}) \, d\vec{r} \tag{2}$$

$$V = \int v(r) \, \psi^*(\vec{r}) \, \psi(\vec{r}) \, d\vec{r} \tag{3}$$

$$U = \frac{1}{2} \int \frac{1}{|\vec{r}-\vec{r}'|} \psi^*(\vec{r}) \psi^*(\vec{r}') \psi(\vec{r}') \psi(\vec{r}) \, d\vec{r} \, d\vec{r}' \tag{4}$$

The electronic density of ground state ψ is given by

$$n(r) = (\psi, \, \psi^*(r)\psi(r) \, \psi) \tag{5}$$

which is clearly a functional of $v(r)$.

Now it has to be shown that conversely $v(\vec{r})$ is a unique functional of $n(\vec{r})$ apart from a trivial additive constant.

Proof : Assume another potential $v(\vec{r})$ with ground state ,
giving rise to the same density $n(\vec{r})$. $\psi' \neq \psi$ since they
satisfy different Schrodinger eqn. unless $v'(\vec{r}) - v(\vec{r}) =$
constant. Hence if we denote the Hamiltonian and the ground
state energies associated with ψ and ψ' by H,H' and E,E'
respectively, from the minimal property of ground state we
get,

$$E' = (\psi',H' \psi') < (\psi,H' \psi) = (\psi, H + V' - V) \psi)$$

or, $E' < E + \int [v'(\vec{r}) - v(\vec{r})] n(\vec{r}) d\vec{r}$ \hfill (6)

Similar arguments by interchanging primed and unprimed
quantities will lead to

$$E < E' + \int [v(\vec{r}) - v(\vec{r})] n(\vec{r}) d\vec{r} \tag{7}$$

Addition of eqns. (25) and (26) yields

$$E - E' < E - E' \tag{8}$$

which is an absurdity. Thus $v(\vec{r})$ is (to within a constant)
a unique functional of $n(\vec{r})$, since in turn $v(r)$ fixes H we
see that the full many particle ground state is a unique
functional of $n(r)$.

Since ψ is a functional of $n(\vec{r})$, so are evidently
the kinetic and interaction energies. So one can define
a functional

$$F[n(\vec{r})] = (\tilde{\psi}, (T+U)\tilde{\psi}) \tag{9}$$

which is a universal functional, valid for any number of particles which is again a functional of $n(\vec{r})$.

For a given potential $v(\vec{r})$, the energy functional is defined as

$$E_V[n] = \int v(\vec{r}) \, n(\vec{r}) \, d\vec{r} + F[n] \tag{10}$$

For the correct $n(\vec{r})$, $E_V[n]$ equals the ground state energy.

Now it has to be shown that $E_V[n]$ is a minimum for the correct $n(\vec{r})$ thereby yielding the ground state energy through a variational scheme. The admissible class of functions are restricted by the condition

$$N[n] = \int n(\vec{r}) \, d\vec{r} = N \tag{11}$$

For a system of N-particles the energy functional of ψ' is given by

$$\varepsilon_V[\psi'] = (\psi', V \psi') + (\psi', (T+U) \psi') \tag{12}$$

It is well known that $\varepsilon_V[\psi']$ has a minimum at the correct ground state ψ relative to arbitrary variation under the condition that the total number of particles is constant. For a given external potential $v(\vec{r})$

$$\varepsilon_V[\psi'] > \varepsilon_V[\psi]$$

with the help of eqns. (9) and (12) one can write

$$\int v(\vec{r}) \, n'(\vec{r}) \, d\vec{r} + F[n'] > \int v(\vec{r}) \, n(\vec{r}) \, d\vec{r} + F[n] \qquad (13)$$

where $n'(\vec{r})$ corresponds to state ϕ'. Equation (13) establishes the minimal property of the energy functional with respect to the density. This provides the basis for the variational scheme in this formalism.

2.1.2 Local density approximation :

The basic idea is to assume local uniformity in an infinitesimal volume element of the co-ordinate space and use the well known expressions of kinetic energy, exchange and correlation energy for the uniform electron gas within that volume element added with the first term in the gradient expansion of the energy functional. So it can be understood that such approximation might work well only when the density is slowly varying in space.

From eqn. (10) we can further separate out the classical coulomb energy and write

$$E_v[n] = \int v(\vec{r}) \, n(\vec{r}) \, d\vec{r} + \tfrac{1}{2} \int \int \frac{n(\vec{r}) \, n(\vec{r'})}{|\vec{r} - \vec{r'}|} \, d\vec{r} \, d\vec{r'} + G[n] \quad (14)$$

where $G[n]$ is another universal functional containing kinetic exchange and correlation energy.

Now G[n] can be expanded in terms of a general gradient expansion, the first two terms of which we generally use

$$G[n] = \int g_0(\vec{r}) \, d\vec{r} + \int g_2(\vec{r}) \, | \nabla n(r) |^2 \, d\vec{r} + \ldots \ldots \quad (15)$$

In this approximation the first term can be written as

$$\int g_0(\vec{r}) \, d\vec{r} = \int t(n) \, n(\vec{r}) \, d\vec{r} + \int \varepsilon_{xc}(n) \, n(\vec{r}) \, d\vec{r} \quad (16)$$

where $t(n) = \frac{3}{10} (3\pi^2 n)^{2/3} = \frac{1.105}{r(n)^2}$

$\varepsilon_{xc}(n) = \varepsilon_x(n) + \varepsilon_c(n)$

$\varepsilon_x(n) = -\frac{3}{4} (\frac{3n}{\pi})^{1/3} = -\frac{0.458}{r_s(n)}$

$r_s(n) = (\frac{3}{4\pi n})^{1/3}$

For $\varepsilon_c(n)$ different expressions are available starting from that of Wigner[28] to the most recent one by Gunnarson, Lundqvist and Lundqvist[29]. For reasons to be stated later, we used the expressions provided by Nozieres and Pines[30].

$$\varepsilon_c = -0.0575 + 0.0155 \ln r_s(n) \quad (17)$$

One can identify $t(n)$, $\varepsilon_x(n)$ and $\varepsilon_c(n)$ as the kinetic exchange and the correlation energy per electron of a uniform electron gas of density n. For further convenience it has also been expressed in terms of local electron liquid parameter $r_s(n)$, i.e. the radius corresponding to the

sphere containing one electron. In our step model we use this approximation for G without the gradient term to be discussed in the next section.

2.1.3 The Gradient Term :

The contribution to the gradient term can be separated into two parts (a) that coming from kinetic energy and (b) that coming from exchange and correlation energy.

$$g_2(r) = g_{xc}^{(2)} [n(r)] + \frac{\lambda}{8\,n(r)} \tag{18}$$

λ is a parameter in the kinetic energy contribution to the eqn. (18) which was originally proposed by Von Weizsacker[31] with $\lambda = 1$. This form has been extensively used in the literature. Jones and Young[32] have compared the response fuhction obtained from the truncated gradient expansion with variable coefficient λ to the Lindhard response function. They found that choosing $\lambda = 1$ yields the correct response for perturbations whose wavelength of importance is small with respect to the Fermi wavelength, while $\lambda = \frac{1}{9}$ is appropriate for perturbations whose wavelength is large with respect to the Fermi wavelength. Thus, choosing $\lambda = \frac{1}{9}$ we would expect the induced screening charge to be relatively accurate at distances far from nuclei or ion but relatively inaccurate at distances near to it. Hodges[33] et al have recently

determined the next term in the gradient expansion eqn.(15)
as contribution from kinetic energy.

$$T_4[n(\vec{r})] = \frac{(3\pi^2)^{2/3}}{540} \int n^{1/3} [(\frac{\nabla^2 n}{n})^2 - \frac{9}{8} (\frac{\nabla^2 n}{n}) (\frac{\nabla n}{n})^2 + \frac{1}{3}(\frac{\nabla n}{n})^4]d\vec{r}$$

(19)

But unfortunately it was found by Wang[34] et al that inclu-
sion of this term increases the deviation to +5 percent from
kinetic energy estimated by Hartree Fock Method for noble
gases. If this term is dropped then it remains within less
than ±1.0 percent. So in this study we ignore this term.

The exchange and correlation contribution to the gradient
term has undergone an intensive investigation in recent years
through the studies of Sham, Herman, Rasolt et al and
Rajagopal and this author[24]. The results of the last two
investigations are the latest and agree in general with
each other. Since the results of this investigation have
already been published we will include the details of this
work only in appendix. In this study an exact and a varia-
tional solution of the electron scattering vertex equation
has been obtained. From these, one can arrive at the
static density correlation function to find out $g_{xc}^{(2)}$, i.e.
the exchange and correlation contribution to g_2 of the
gradient term of eqn. (9). We apply this general expre-
ssion of $g_{xc}^{(2)}$ to Yukawa type of interaction of electrons

with a screening parameter ξ. In the large^3 limit the varia-
tional result coincides with the exact result but for

$\xi \rightarrow 0$, i.e. strictly coulomb limit there is a logarithmic
divergence for the exact result. In place of using Thomas-
Fermi expression for ξ if one uses a self consistent ξ
from the longitudinal dielectric function our results agree
with that of Sham in the high density limit and that of
Kleinnan for $\pi k_F \rightarrow 0$ (low density).

$$g_{xc}^{(2)} = c \; (r_s) \; n^{-4/3}$$

A plot of $c(r_s)$ vs r_s has been provided by Rasolt[24]. In our
continuous density model of alloy we use the local density
approximation along with the gradient terms discussed above.

2.1.4   Exact Kinetic Energy Formulation :

In this formulation of the density functional method
Kohn and Sham[3] found a way to avoid the local density appro-
ximation for the kinetic energy as follows :

Suppose for a given $v(\vec{r})$, $n(\vec{r})$ is the correct density
corresponding the ground state energy $E_v[n(\vec{r})]$ from eqn.
(14). If we allow an arbitrary variation of $n(\vec{r})$ subject
to the condition that $\int \delta \, n(\vec{r}) \, d\vec{r} = 0$ the minimal property
of the ground state energy demand, that $\delta \, E_v[n] = 0$ or in
another way it can be expressed as

$$\int \delta\, n(\vec{r}) \cdot [\frac{\delta\, E_V}{\delta n(\vec{r})} - \varepsilon]\, d\vec{r} = 0 \tag{20}$$

for arbitrary $\delta\, n(\vec{r})$ subject to the restrictive condition stated above. ε is a Lagrange multiplier.

$$\frac{\delta\, E_V}{\delta\, n(\vec{r})} = \phi(\vec{r}) + \frac{\delta\, T_s[n]}{\delta\, n(\vec{r})} + \mu_{xc}(n(\vec{r})) = \varepsilon \tag{21}$$

where $\quad \phi(\vec{r}) = v(\vec{r}) + \int \frac{n(\vec{r})}{|\vec{r}-\vec{r}'|}\, d\vec{r}' \tag{22}$

and $\quad \mu_{xc}(n) = \frac{\delta}{\delta n(\vec{r})} (G[n] - (\phi, T\phi)) = \frac{dE_{xc}}{dn} = \frac{d}{dn}(n\varepsilon_{xc}(n))$
$$\tag{23}$$

$E_{xc}[n]$ is the exchange and correlation contribution to the $G[n]$ and can be written approximately as

$$E_{xc}[n] = \int n(\vec{r})\, \varepsilon_{xc}[n(\vec{r})]\, d\vec{r} \tag{24}$$

with $\varepsilon_{xc}[n]$ the exchange and correlation energy per electron of a uniform electron gas of density n. This gives a thermodynamic meaning to μ_{xc} in the sense that it is the exchange and correlation contribution to the chemical potential.

Equation (20) written in operator form looks like an one particle Schrodinger equation.

$$[- \tfrac{1}{2}\Delta^2 + [\phi(\vec{r}) + \mu_{xc}[n(\vec{r})]]\, \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}) \tag{25}$$

with $\quad n(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 \tag{26}$

where N is the number of electrons. The set of equations
(22), (23), (25) and (26) can be solved self consistently
to get ε_i's and $n(\vec{r})$ which in turn will yield the ground
state energy as given below.

$$E = \sum_{i=1}^{N} \varepsilon_i - \tfrac{1}{2} \int \int \frac{n(\vec{r}) \; n(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' + \int n(\vec{r})[\varepsilon_{xc}(n(\vec{r}))$$
$$- \mu_{xc}[n(\vec{r})]] \, d\vec{r} \qquad (27)$$

where the second term is due to double counting of electron-
electron repulsion term.

The above procedure has been used in this study in the
last chapter to find out the cohesive energies of pure
metals and the heat of solution of alloys from the point of
view of a pseudo-atom approach which will be discussed in
detail there.

2.2 Density Functional Scheme and the Neutral Pseudo-atom Concept

We briefly outline here the various ways in which the
density functional scheme can be implemented for calculating
the ground state energy of pure metals and alloys. Many of
these are best understood in terms of a neutral pseudo-
atom idea. We first discuss the pure metal case, and then
the alloy. Details are given in Chapters 3 and 4.

a) Pure metal :

The most direct method, followed by Janak et al[35] is to start with an external potential $v(\vec{r})$ (periodic), solve the Kohn Sham one electron equation using one of the methods standard in band theory, determine energy levels E_{nk} and wave functions $\psi'_{nk}(r)$, construct $n(\vec{r})$ $(= \sum_{n,k} \psi_{nk}(r)^2)$ and thence r_{eff} $(n(r))$ and iterate to self-consistency. This has been done, with $v(\vec{r}) = \sum_{l} \dfrac{-Z}{|\vec{r} - \vec{R}_l|}$ where Z is the nuclear charge, by Janak et al for transition metals with great success. Clearly the method avoids all assumptions about the ionic potential: the only approximations made are in the density functional form. However, the method is computationally prohibitive, and physically not very illuminating.

In general, the density $n(\vec{r})$ can be written

$$n(\vec{r}) = n_0 + \sum_{j} \delta n(\vec{r} - \vec{R}_j) \tag{28}$$

where n_0 is the average density, and in a pure metal

$$\int \delta n(\vec{r}) \, d\vec{r} = 0 \tag{29}$$

This form suggests the following two approaches.

i) Since $n(\vec{r})$ is periodic

$$n(\vec{r}) = n_0 + \sum_{K} n_K \, e^{i\vec{K} \cdot \vec{r}} \tag{30}$$

$\vec{K}$ being the reciprocal lattice vectors of the lattice. Thus in a crystal, the energy is a function of the discrete set of variables $(n_0, [n_{\vec{K}}])$. One knows the functional form for $[n_{\vec{K}}] = 0$ (uniform electron gas), and the form for small $[n_{\vec{K}}]$ (power series in $n_{\vec{K}}$). So, if $n_{\vec{K}}/n_0 \lesssim 1$, one can proceed as follows :

The H-K eqn. (10) gives the ground state energy functional as

$$E = \int v(\vec{r})\, n(\vec{r})\, d\vec{r} + F[n(\vec{r})]$$

$$= n_0 \int v(\vec{r})\, d\vec{r} + \sum_K v_{-\vec{K}}\, n_{\vec{K}} + F(\bar{n}, n_{\vec{K}}) \qquad (31)$$

where $v(\vec{r})$ is the sum of the ionic potentials and F is the energy of interacting electron gas. If $n_{\vec{K}}$'s are small then one can expand F in a Taylor series as

$$F(n_0, n_{\vec{K}}) = F(n_0) + \tfrac{1}{2} \sum_K n_{\vec{K}}\, n_{-\vec{K}} \left(\frac{\partial^2 F}{\partial nK\, \partial n_{-K}}\right)\Big|_{n_K} = 0 + \cdots\cdots$$

$$= F(n_0) + \tfrac{1}{2} \sum_K n_{\vec{K}}\, n_{-\vec{K}}\, \mathcal{X}_K + \cdots\cdots \qquad (32)$$

The term linear in n_K is absent because n_0 is the mean valence density and so $\delta n(r)$ integrates to zero.

Minimizing E with respect to $n_{\vec{K}}$ from eqn. (3) after substituting eqn. (4) for F we get,

$$n_K = - \frac{v_{\vec{K}}}{\mathcal{X}_{\vec{K}}(n_0)} \qquad (33)$$

We note that $n_{\vec{K}}$ is small if (i) $v_{\vec{K}}$ is small $z$nand (ii) the electron gas responds weakly. Putting this $n_{\vec{K}}$ from eqn. (5) into eqn. (3) we get the ground state energy

$$E = \int v(\vec{r}) \; n_0 \; d\vec{r} + F(n_0) - \tfrac{1}{2} \sum_{\vec{K}} \frac{|v_{\vec{K}}|^2}{\chi_{\vec{K}}(n_0)} \qquad (34)$$

In linear response theory the last term of eqn. (34) is identical with the second order perturbation term in energy in pseudopotential perturbation theory.

The above derivation shows the unity in two apparently diverse approach and the separability of energy contribution due to the uniform and the periodic component in the domain of validity of perturbative treatment i.e. $n_{\vec{K}}$ small.

ii) The neutral pseudo-atom approach. The idea is to develop an expansion for $\delta n(\vec{r}-\vec{R}_j)$. Clearly, the major role in determining $\delta n(\vec{r}-\vec{R}_j)$ will be played by the potential in the Wigner Seitz Cell j. Since for $\vec{r}$ within this cell, the potential is strong. The effect of other cells is very small because the ionic potential is nearly completely screened by the electrons; the residual effect is weak and of short range. So, one determines $\delta n(\vec{r}-\vec{R}_j)$ non perturbatively in so far as the effect of $v(\vec{r}-\vec{R}_j)$ and the screening charge in the cell j are concerned. Such a programme can be implemented in two ways.

ii α) Parametric method :

We parametrize $\delta n(\vec{r})$ suitably, and use a known density functional form, e.g. the local form plus gradient terms. This method is non perturbative in the sense that $\delta n(\vec{r})$ is not a priori assumed small; it is variationally determined. The method is discussed in detail in Chapter 3 and is applied there to some simple metals. It turns out that the effect of other cells on $\delta n(\vec{r}-\vec{R}_j)$ is negligible, occuring only via the electrostatic interaction term in $E[\,n\,]$.

ii β) Kohn Sham method :

As stated above, one can obtain an approximate expression for $\delta n(\vec{r}-\vec{R}_j)$ by neglecting the effect of other cells. The effect of the cell j (i.e. $v(\vec{r}-\vec{R}_j)$ and the effect of electron density n_0 inside cell j, and of $\delta n(\vec{r}-\vec{R}_j)$) is considered 'exactly', i.e. we solve the Kohn Sham equation for the appropriate $v_{eff}(\vec{r}-\vec{R}_j)$, obtain wave functions $\psi(\vec{r}-\vec{R}_j)$, construct $\delta n(\vec{r}-\vec{R}_j)$ and iterate to self consistency. (See Chapter 5 for details). From the $n(r)$ so obtained $E[\,n\,]$ can be calculated. However, here again, the effect of two centre terms is calculated perturbatively, i.e.

$$E[n_0 + \sum_j \delta n(\vec{r}-\vec{R}_j)]$$
$$\text{two center}$$

$$= \tfrac{1}{2} \sum_{j \neq 1} \delta n(\vec{r}-\vec{R}_j)\, \delta n(\vec{r}-\vec{R}_1) \times \frac{\partial^2 E}{\partial n(\vec{r}-\vec{R}_j)} \, \partial n(\vec{r}-\vec{R}_1) \Bigg|_{\delta n = 0} \quad (35)$$

Such a calculation was first carried through by Dagens[9]. We present a systematic theory in Chapter 5 which avoids the introduction of arbitrary form factors as done by Dagens[9], and can be used to study the errors introduced in the approximations made.

b) Alloy :

The problem of applying the density functional formalism clearly, in alloys, the procedure used by Janak[35] et al for pure metals is inapplicable. However, if the ion potential (pseudopotential) is weak, the ground state energy can be calculated by perturbation theory as described in Chapter 1. The use of linear response theory to describe the effect of charge contrast ($Z_A - Z_B \neq 0$) on the electron gas is questionable. However, since the effect of an impurity ion is strongly localized, we can u e the neutral pseudo-atom idea.

Consider the case of alloy where neutral atom of solute A is dissolved in(the site at origin) solvent B. In the similar way as it was done for the pure metal case we can start with a rigid jelly of electron of mean valence density n_B corresponding to that of B. Then we put in the origin the solute ion with the excess electrons or holes over the valency of B and the B ions at other sites. Now if the electrons are allowed to relax the B-ions will be

independently screened but near the A-site two phenomena will take place (i) the screening of the solute ion A and (ii) the alloying i.e. attaining thermo-dynamic equilibrium by equalisation of chemical potential throughout the system. If n_A and $\delta\, n_A^o$ are the mean valence density of electrons and the screening charge polarisation in pure A respectively and n_B^o and $\delta\, n_B^o$ . . are those corresponding to pure B then the charge polarisation of the electrons over n_B^o in the neutral A atom in the alloy will be different from $n_A^o - n_B^o + \delta\, n_A^o$ because of the effect of alloying. The charge distribution in the alloy can be written as

$$n(\vec{r}) = n_B^o + \delta\, n_{AB}(\vec{r}) + \sum_{j \neq 0} \delta\, n_B^o(\vec{r}-\vec{R}_j) \tag{36}$$

Note here that

$$\int \delta\, n_{AB}(\vec{r})\, d\vec{r} = Z_A - Z_B \text{ in place of zero for the pure case.}$$

Z_A and Z_B are the valencies of the solute A and the solvent B respectively. In pure metals the charge polarisation due to screening gives rise to a weak interaction between the nearest neighbors ($\leq$ 4 percent of the energy of the neutral atom for Alkali Metals[9])but in the alloy it will not be small around the solute atoms because charge transfer will cause $\delta\, n_{AB}(\vec{r})$ to extend into the neighboring neutral atom cells with magnitude depending on the difference in the chemical potential.

In a parametric variational approach our attempt is to simulate the $\delta n_{AB}(\vec{r})$ by discontinuous and continuous functions in the step model and the tangent hyperbolic model respectively (See Chapter 3).

The equation (36) can be rewritten as

$$n(\vec{r}) = n_B(\vec{r}) + n_{loc}(\vec{r}) \tag{37}$$

where $n_B(\vec{r}) = n_B^0 - n_B^0 \, \Theta \, (R_B - \| \vec{r} \|) + \sum_{l \neq 0} \delta \, n_B^0(\vec{r}-\vec{R}_l)$

$n_{loc}(\vec{r}) = n_B^0 \, \Theta \, (R_B - \| \vec{r} \|) + \delta \, n_{AB}(\vec{r})$

The atomic radius of pure B and its lattice vectors are given by R_B and R respectively and n_B is the density of electrons of the pure solvent as it takes part in the alloy. $n_{loc}(\vec{r})$ represents the electron density in the solute atom as it exists in the alloy. Here we assume a spherical Wigner-Seitz cell for the solvent with a radius R_B in place of a polyhedra. This is quite a good approximation for close packed structure although the electrostatic energy estimated will be slightly different from that determined by the Ewald method for a polyhedra. This will be discussed in more details in Chapter 5. The advantage of this separation of $n(\vec{r})$ into $n_B(\vec{r})$ and $n_{loc}(\vec{r})$ is that the heat of solution of the alloy can be written primarily as a difference between the energy of A-pseudo-atom as it exists in the

alloy and the energy of an A pseudo-atom as it exists in the pure solid. Otherwise if the heat of solution is written as the difference in the energy of all the constituent atoms to that of all the participating atoms in their pure solid state it poses a problem of evaluating two large energies and the errors involved may make the estimate of the heat of solution totally unreliable.

In the Kohn Sham version of the density functional scheme, $\delta n_{AB}(\vec{r})$ is obtained by self consistently solving on one centre Schrodinger like equation, with $v(\vec{r}) = v_A(\vec{r})$ and the other coulomb potential terms arising from the electron charge Z_A composed of Z_B distributed in the WS cell with density n_B^o and $Z_A - Z_B$ distributed with density $\delta n_{AB}(\vec{r})$. Knowing $\delta n_{AB}(\vec{r})$, one can calculate the ground state energy of the alloy (see Chapter 5, Section 2).

2.3 The Heat of Solution of Alloys

When we refer to the heat of solution $\Delta \bar{\bar{H}}_A$ in this study it always refers to the partial heat of solution per atom (the equivalent of partial molal heat of solution in the conventional thermodynamic term). If $n(\vec{r})$ is the charge density distribution in the alloy and $E[n(\vec{r})]$ gives its ground state energy, the heat of solution per atom of solute is given by

$$\bar{H}_A = E[n(\vec{r})] - M\, F_B - E_A \tag{38}$$

where M is the number of solvent atoms B with valency Z_B
alloyed with 1 atom of A with valency Z_A. E_B and E_A are
the ground state energies per atom of pure solid solvent B
and solute A respectively. The form of eqn. (38), although
correct, is not convenient for calculating the heat of
solution for the reasons mentioned at the end of the last
section. So we try to write

$$E[n(\vec{r})] = M\, E_B + E_A^{alloy} \tag{39}$$

so that,

$$\Delta \bar{H}_A = E_A^{alloy} - E_A \tag{40}$$

where E_A^{alloy} may be thought of as the energy of the solute
atom A in its configuration in the alloy. Now the problem
reduces to partitioning $E[n(\vec{r})]$ as given in eqn. (39). Then
the evaluation of the heat of solution by eqn. (40) becomes
quite straightforward.

Following eqn. (14) one can write

$$E[n(\vec{r})] = \int v(\vec{r})\, n(\vec{r})d\vec{r} + \tfrac{1}{2}\int \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' + G[n(\vec{r})] + V_{ii} \tag{41}$$

where V_{ii} is the electrostatic interaction energy between
the ions and G is the universal functional of $n(\vec{r})$ containing

the kinetic, exchange and the correlation energy functional as already defined in the first section.

Here the potential in the $v(\vec{r})$ is given by

$$v(\vec{r}) = v_A(\vec{r}) + \sum_{1 \neq 0} v_B(\vec{r}-\vec{R}_\ell) \tag{42}$$

where $v_A(\vec{r})$ is the potential of the A-ion at the origin and $v_B(\vec{r}-\vec{R})$ is the potential of the B-ion at the site with lattice vector $\vec{R}_\ell$. Although in this study we will use the model potentials for both v_A and v_B, it is not a feature of this formalism by any means. For a rigorous calculation one should use potentials constructed from the first principles computations of the atomic structure as is customary in the different band structure calculations.

Following the discussion in the last section the charge density in the alloy can be written as

$$n(\vec{r}) = n_B(\vec{r}) + n_{loc}(\vec{r}) \tag{43}$$

Putting equations (42) and (43) in the eqn. (41) one gets

$$E[n(\vec{r})] = \sum_{1 \neq 0} v_B(\vec{r}-\vec{R}_\ell)\, n_B(\vec{r})\, d\vec{r} + \tfrac{1}{2} \frac{n_B(\vec{r})n_B(\vec{r})}{|\vec{r}-\vec{r}'|}\, dr\, dr' +$$

$$G[n_B] + \sum_{\substack{j \neq 1 \\ j1 \neq 0}} \frac{Z_B^2}{2} \frac{1}{|\vec{R}_j-\vec{R}_1|}$$

$$+ \int v_A(\vec{r}) n_{loc}(\vec{r}) \, d\vec{r} + \tfrac{1}{2} \int \frac{n_{loc}(\vec{r}) \, n_{loc}(\vec{r}')}{|\vec{r}-\vec{r}'|} \, d\vec{r} \, d\vec{r}' + G[n(\vec{r})] -$$

$$- G[n_B(\vec{r})]$$

$$+ \int v_A(\vec{r}) \, n_B(\vec{r}) \, d\vec{r} + \int \frac{n_{loc}(\vec{r}) \, n_B(\vec{r}')}{|\vec{r}-\vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$+ \oint \sum_{1 \neq 0} v_B(\vec{r}-\vec{R}) \, n_{loc}(\vec{r}) + Z_A \sum_{1 \neq 0} \frac{Z_B}{|\vec{R}_1|} \qquad (44)$$

Since $n_B(\vec{r})$ is the correct ground state density of the assembly of M atoms of pure solvent, the first four terms in eqn. (42) gives ME_B. The next four terms are primarily one centre contributions originating from the pseudo-atom A as it exists in the alloy. It also includes a small contribution from the effect of environment of B on the kinetic, exchange and the correlation energies of the pseudo-atom A.

The last four terms represent the electrostatic interaction between the pseudo-atom A with the surrounding B-pseudo-atoms and so are two centre contributions. Since these terms contain long range functions we rewrite them in a form in which the long range parts explicitly cancel. These are computationally suitable for an empty core pseudopotential both for A and B.

$$\int v_A(\vec{r}) \, n_B(\vec{r}) \, d\vec{r} = -Z_A \int \frac{n_B(\vec{r})}{|\vec{r}|} \, d\vec{r} \qquad (45)$$

Since $n_B(\vec{r}) = 0$ by definition within the core radius of A. Again,

$$\int \frac{n_{loc}(\vec{r})\, n_B(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' = \oint \frac{n_B(\vec{r}')}{|r'|}\, d\vec{r}' \int_0^{r'} n_{loc}(\vec{r})\, d\vec{r}$$

$$+ \frac{n_{loc}(\vec{r})}{|\vec{r}|} \int_0^r n_B(\vec{r}')\, d\vec{r}'$$

$$= \int \frac{Q_{loc}(\vec{r}')\, n_B(\vec{r}')}{|\vec{r}'|}\, d\vec{r}' + \oint \frac{Q_B(\vec{r})\, n_{loc}(\vec{r})}{r}\, d\vec{r}$$

$$= Z_A \int \frac{n_B(\vec{r}')}{|\vec{r}'|}\, d\vec{r} + \int \frac{[Q_{loc}(r') - Z_A]}{r'}\, n_B(\vec{r}')\, d\vec{r}' + \int \frac{Q_B(\vec{r}) n_{loc}(\vec{r})}{r}\, d\vec{r}$$

$$(46)$$

where $Q_B(r) = \int_0^r n_B(\vec{r})\, d\vec{r}$ and $Q_{loc}(r') = \int_0^{r'} n_{loc}(\vec{r}')\, d\vec{r}'$

Adding eqns. (43) and (44) we get

$$\oint v_A(\vec{r})\, n_B(\vec{r})\, d\vec{r} + \oint \frac{n_{loc}(\vec{r})\, n_B(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' = n_B^0 \int_{R_B} [\frac{[Q_{loc}(r)-Z_A]}{r} d\vec{r}'$$

$$+ \int \frac{Q_B(r)\, n_{loc}(\vec{r})}{r}\, d\vec{r} \qquad (47)$$

where we have neglected δn_B^0 as defined in the last section and so we can write

$$Q_B(r) = 0 \text{ for } r < R_B$$

$$= \frac{4\pi}{3} (r^3 - R_B^3)\, n_B^0 \text{ for } r > R_B \qquad (48)$$

The justification for ignoring δn_B^o or otherwise will be provided by the results of our calculation of cohesive energy for pure elements assuming a cosine function for δn_B^o with some parameters to be determined variationally from the minimal property of the ground state energy. The estimate of the amplitude of this cosine function will show how much we are justified in the above assumption in different cases.

The eqn. (47) is clearly in a computationally suitable form as both the integrals reduce to zero beyond a certain distance.

The last two terms in eqn. (44) can also be/recast as

$$\int \sum_{\ell \neq 0} v_B(\vec{r} - \vec{R_1}) \, n_{loc}(\vec{r}) \, d\vec{r} = -\int n_{loc}(\vec{r}) \, d\vec{r} \sum_{1 \neq 0} \frac{Z_B}{r - R} + \int n_{loc}(\vec{r}) \sum_{1 \neq 0} V_{loc}(\vec{r} - \vec{R_1}) d\vec{r}$$

with $\qquad v_{loc}(\vec{r}) = -(Z_B/r)\, \theta(r_o^B - r)$

where r_c^B is the core radius of solvent B and $v_{oc}(r)$ is a located function. The first integral in the L.H.S. of eqn. (47) can be written as

$$- Z_B \int \frac{r\, n_{loc}(\vec{r}) \cdot \mathcal{P}_B(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' = - \sum_{1 \neq 0} \frac{[Q_{loc}(\vec{R}) - Z_A]}{|R|} \cdot Z_B$$

$$+ \int d\vec{r} \, \frac{n_{loc}(\vec{r})}{r} \{ Z_B \sum_{1 = 0} \theta(\vec{r} - \vec{R}) \} - Z_A \sum_{1 \neq 0} \frac{Z_B}{R} \qquad (50)$$

The last term of eqn. (50) cancels with the last term of eqn. (42) and finally taking eqns. (41), (47), (49), (50) and (40) together we can write the final expression for the heat of solution $\Delta \bar{H}_A$ as

$$\Delta \bar{H}_A = \int v_A(\vec{r}) \, n_{loc}(\vec{r}) \, d\vec{r} + \frac{1}{2} \int \frac{n_{loc}(\vec{r}) \, n_{loc}(\vec{r}')}{|\vec{r}-\vec{r}'|} \, d\vec{r} \, d\vec{r}' + $$

$$+ G[n(\vec{r})] - G[n_B^o]$$

$$+ n_B^o \int_{R_B} \frac{[Q_{loc}(r) - Z_A]}{r} \, d\vec{r} + \int \frac{Q_B(r) n_{loc}(\vec{r})}{r} \, d\vec{r}$$

$$+ \int n_{loc}(\vec{r}) \sum_{\ell} v_{loc}(\vec{r}-\vec{R}_\ell) d\vec{r} - \sum_{\ell \neq 0} \frac{[Q_{loc}(R_\ell) - Z_A] Z_B}{|R_\ell|}$$

$$+ \int n_{loc}(\vec{r}) \, d\vec{r} \, \{Z_B \sum_{\ell} \alpha(|\vec{r}| - |\vec{R}_\ell|)\} - E_A \tag{51}$$

This expression contains all short range terms only. $n_{loc}(\vec{r})$ by its construction is short range. So, the first two terms, the sixth, seventh and the ninth terms of eqn. (51) is short range. $Q_{loc}(r)$ appearing in the fifth and the eighth terms goes to Z_A fast enough for distances somewhat greater than R_B rendering both of these terms also short range. $G[n(\vec{r})] - G[n_B^o]$ if expanded also leads to residual short range terms making the eqn. (51) totally short range.

We use this expression for the heat of solution for the parametric variational scheme described in the next chapter. But for the Kohn-Sham scheme we use a different version of the same formulation without assuming δn_B^O negligible to be described in Chapter 5.

Chapter 3

Parametric Variational Method

Here we describe the ground state density of the electrons in the alloy by a function involving free parameters in it and compute the ground state energy from its minimal property with respect to the density variation i.e. the variation of these free parameters. From this alloy ground state energy one subtracts the ground state energy of the components to get the heat of solution of the alloy.

It is obvious that any approach to the heat of solution of alloys has to be preceded by a treatment of the ground state energy of the pure constituents within its scheme. Also, for understanding the physics of the alloy problem it constitutes logical path to follow. So we start this chapter with a discussion on the calculation of the ground state energy of pure metals – its promises and pitfalls, to provide for the necessary orientation to go to the alloy problem.

The discussion on alloy problem will start with a a uniform density model for the components with different valencies resulting into a step in the alloy electron density. The two parameters in the density will be the size and the position of the step one of which can be determined

from the conservation of charge. The other parameter acts
as the free one with respect to which the energy is mini-
mised. This is essentially a one parameter variational
model for the alloy. This model is quite insufficient for
the treatment of the alloy for reasons to be mentioned in
this section but it is an extremely simple model bringing
out some aspects of the alloying phenomenon seen from expe-
rimental studies so far.

In the above model the gradient term in the density
functional expansion of the energy will have to be neglected
because the discontinuity in $n(\vec{r})$ at the step will make
this term singular. To take into account this term (which is
by no means negligible) we model the density with a conti-
nuous tangent hyperbolic function with three parameters one
of which will be determined by charge conservation. Thus
this is a model with two free parameters with respect to which
energy will be minimised. The distribution being physically
quite similar to the step model, this can be thought of as a
model which allows the electrons to relax from the step
configuration with the help of the driving force provided
by the gradient term. The inadequacies of this model will
be brought out in this section for a clear understanding of
the directions for future effort. The discussion on the

computational results of these models will be postponed till the next chapter where we will discuss the systematic trends in the heat of solution of the alloys.

3.1   Calculation of ground state energy of pure metals

From eqn. (14) of Chapter 2 one can write the ground state energy E_g of a system with the ground state density of electrons $n(\vec{r})$ as

$$E_g[n] = \int v(\vec{r})\, n(\vec{r})\, d\vec{r} + \tfrac{1}{2} \int\int \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}\, d\vec{r}' + G[n] \quad (1)$$

where $G[n]$ is a universal functional of density $n(\vec{r})$ containing the kinetic, exchange and correlation energy contributions. This equation shows that the problem of calculating E_g is essentially one of arriving at a correct $v(\vec{r})$ and $n(\vec{r})$ for the ground state of the system. For $v(\vec{r})$ we choose the Ashcroft local empty core model pseudopotential as it yields the cohesive energy value of the real systems quite in agreement with their experimental value. This indicates that empty core pseudopotential may provide a sufficiently good model potential for our purpose.

Now the next task is to choose a correct $n(\vec{r})$ with some variational parameter to be determined by the minimal property of ground state energy. Our choices for this purpose and their justifications are described below.

energy has been written as a function of atomic radius which
is related to the size of n_0 for a given Z. The expression
of E_g when minimised with respect to R gives the ground state
energy. By comparing this value R_{min} corresponding to
minimum and the E_g with the experimental value we can get
an idea as to how good is this uniform density assumption
for a particular case.

For the estimation of correlation energy in eqn. (3)
we have used the expression of Nozieres and Pines[30] in place
of more recent ones provided by Hedin[36] et al. This is
because of better correspondence of R_{min} with the observed
value obtained by the use of the expression provided by the
former expression. This aspect we will discuss in the next
chapter along with the calculated results.

For calculating G[n] for this case in eqn. (1) we have
used the local density approximation and completely negle-
cted the gradient term. Incidentally, this is the general
practice for evaluating the structure independent or one centre
term in the pseudopotential perturbation theory where
deviation from uniform density resulting in a periodic compo-
nent is assumed to be small and so treated by linear response
theory. This deficiency can be made up by treating this
deviation along with the uniform component together by the
use of the density functional formalism given by the eqn.(1)

where the gradient term also can be taken into account.
One should also remember that this expression is formally
exact. So the next obvious step is to try to incorporate
such deviation in the parametric density functional forma-
lism to evaluate both one centre and two centre terms accura-
tely.

(b) The periodic density variation : In place of a uniform
density here we take a density distribution in pure metals
incorporating a periodic component also. The form of $n(\vec{r})$
should be such that it is continuous throughout the solid
with no discontinuity in slope which will be unphysical in
the sense that the higher order gradient terms will diverge.
The form of $n(\vec{r})$ which we have chosen for our calculation is
given within a single WS all centred at r = 0 by

$$n(\vec{r}) = n_0 + \sum_l B_l \cos k_l r$$

Since we require that the function and its slopes are con-
tinuous across the Wigner-Seitz cell boundary of r, we have

$$\frac{dn}{dr}\Big|_{r=R} = 0 \quad \text{or} \quad k_l = \frac{l\pi}{R} \tag{4}$$

when R is radius of the W.S cell.

Thus, $n(\vec{r}) = n_0 + \sum_l B_l \cos\left(\frac{l\pi r}{R}\right)$ \hfill (5)

The constraint on $n(\vec{r})$ is that the total charge must be conserved i.e. the system is neutral electrically. So one has in each unit all

$$\int_0^R n(\vec{r}) \, d\vec{r} = Z \qquad (6)$$

Thus, if n periodic density component B_l's are assumed to be non-zero, there are $(n+2)$ parameters (n_o, R_{at}, B_l) out of which one is fixed by the constraint eqn. (6). Since strong density inhomogenities are disfavoured (e.g. via the gradient term), we assume for simplicity that only one B_l, that corresponding to the smallest value $l = I$ is non-zero. In this case the eqn. (6) gives

$$n_o = \frac{3Z}{4\pi R^3} - \frac{3B}{(k.R)^3} [k^2 R^2 \sin kR + 2kR \cos kR - 2 \sin kR] \qquad (7)$$

where $B = B_l$ and $k = k_l$

Now, from eqn. (4) we get $kR = \pi$ and putting it in eqn. (7) n_o is evaluated leaving R and B as two free-parameters to be determined variationally.

With the above two models for calculating the ground state energy of pure components we pass on to the problem of constructing models for alloys in the same spirit.

3.2 Step-Model

In constructing this model we start with the spherical atoms of components with uniform density - both solute and the solvent. From the solvent matrix we remove an atom from the lattice site at origin and put the solute atom there. Fig. 3.1(a) shows the solute atom electron density to be uniformly n_A^o and its radius R_A. Fig. 3.1(b) shows the prepared solvent matrix with the atom at origin removed. The density here is also uniformly n_B^o and its atomic radius is R_B. Here the valency of the solute is taken to be lower than that of the matrix. Now if the solute atom electron distribution is either expanded or compressed to fit into the rigid solvent matrix we arrive at a configuration of the alloy whose density distribution is shown in Fig. 3.1(c). The energy expended in this process is called the size factor energy contribution to the alloying. Still now no electro-chemical interaction between the solvent and the solute has taken place. Now if we start moving the step with two res-trictions namely (a) the electron density of the solvent matrix far away from the solute remains the same as that of the pure component and (b) the charge of the total system is conserved, we can arrive at a configuration given by Fig. 3.1(d) which minimises the energy expressed by eqn. (1). The energy involved in passing from configurations

(a) SOLUTE

(b) SOLVENT
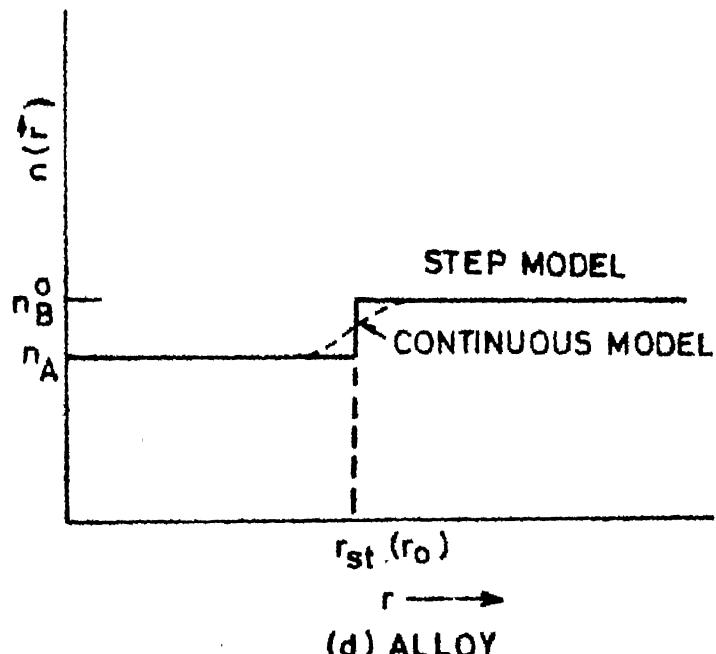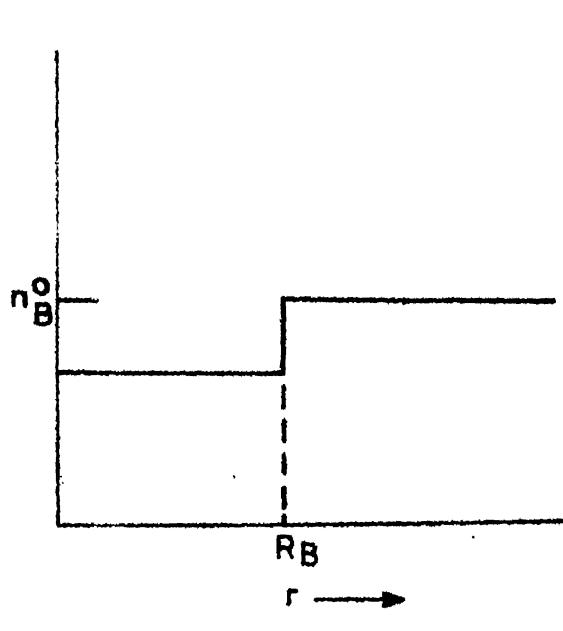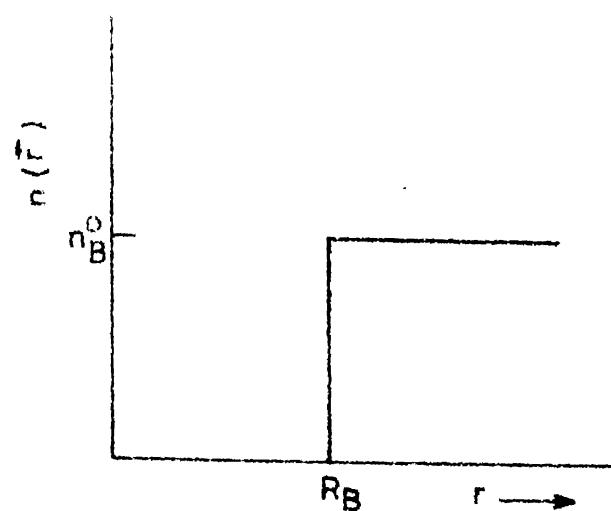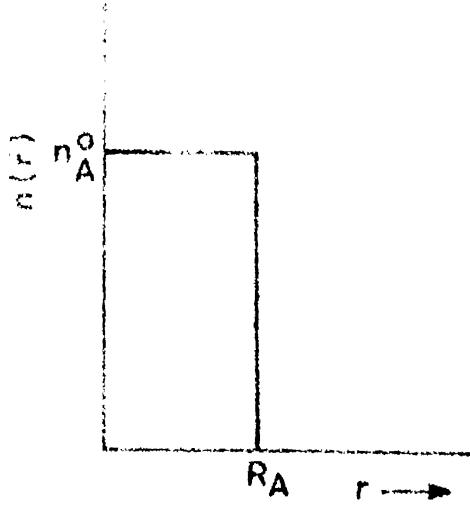
(c) ALLOY

(d) ALLOY

Q 3.1 : SCHEMATIC DIAGRAM FOR THE CHARGE DISTRIBUTION, n(r), OF (a) PURE SOLUTE (A) IN A WS CELL (b) PURE SOLVENT (B) WITH THE WS CELL AT/ORIGIN REMOVED (c) ALLOY WHEN SOLUTE ATOM FITS EXACTLY IN SOLVENT (d) ALLOY FOR ENERGY MINIMUM CONFIGURATION.

correspoi.ding to Fig. 3.1(c) to 3.1(d) is tie electro-chemical contribution to the alloying process resulting in a dipole at the surface between the solute atom and the matrix. This is accompanied by a lowering in energy when alloying is favorable. The density in this model can be expressed by

$$n(\vec{r}) = n_A \; \Theta(r_{st} - \vec{r}) \; n_B^o \; \Theta(\vec{r} - r_{st}) \qquad (8)$$

where r_{st} is the distance from origin of the step and n_A can be found out from the charge conservation as

$$n_A = n_B^o + \frac{3(Z_A - Z_B)}{4\pi r_{st}^3} \qquad (9)$$

where Z_A and Z_B are the valencies of the solute and solvent respectively. Now the density is completely defined in terms of the parameter r_{st}. Following eqn. (49) of Chapter 2 we can proceed to evaluate different terms for finding out the heat of solution.

The pseudopotential contribution, TP1, to E_A^{alloy} embodied in the first term of eqn. (49) of Chapter 2 is given in terms of r_{st} by

$$TP1 = \frac{3Z_A}{2} \left[\frac{Z}{r_{st}} + \frac{r_c^{A^2} Z_B}{R_B^3} - \frac{r_c^{A^2} Z}{r_{st}^3} - \frac{Z_B}{R_B} \right] \qquad (10)$$

where $\Delta Z = Z_B - Z_A$ and r_c is the core radius of Ashcroft local pseudopotential of A at the origin given by

$$v_A(\vec{r}) = 0 \text{ for } r < r_c^A$$

$$= -\frac{Z_A}{r} \text{ for } r > r_c^A \tag{11}$$

The electron-electron interaction term in the expression for E_A^{Alloy} denoted by TC1 is given by

$$TC1 = \begin{cases} \frac{16\pi^2}{15} n_A^2 r_{st}^5 + \frac{16\pi^2}{3} n_B^0 [\frac{3n_B^0 r_{st}^5}{10} + n_B^0 R_B^2(\frac{R_B^3}{5} - \frac{r_{st}^3}{2}) + \frac{r_{st}^3}{2} n_A \\ \qquad\qquad\qquad\qquad\qquad (R_B^2 - r_{st}^2)] \\ \qquad\qquad\qquad\qquad\qquad\qquad \text{if } r_{st} < R_B \\ \frac{3}{10} Z_B \frac{\Delta Z R_B^2}{r_{st}^3} + \frac{16\pi^2}{15} R_B^5 n_B^{0\,2} + \frac{3\Delta Z}{r_{st}} (\frac{\Delta Z}{5} - \frac{Z_B}{2}) \tag{12} \end{cases}$$

$$+ 1.5 \ Z_B \Delta Z \ (\frac{r_{st}^2}{5R^3} - \frac{R_B^2}{5r_{st}^3} + \frac{1}{r_{st}} - \frac{1}{R_B}) \quad \text{for } r_{st} > R_B$$

The kinetic, exchange and correlation contribution to E_A^{alloy} in the local density approximation is given respectively by,

$$TK = \frac{3}{10} (3\pi^2)^{2/3} [V_{st} n_a^{5/3} + n_B^{0\,5/3} (V_B - V_{st})]$$

$$TX = -0.75(\frac{3}{\pi})^{1/3} [V_{st} n_a^{4/3} + n_B^{0\,4/3} (V_B - V_{st})] \tag{13}$$

$$TC = V_{st} n_a \varepsilon_c(n_a) + (V_B - V_{st}) n_B^0 \varepsilon_c(n_B)$$

where $V_{st} = \frac{4\pi r_{st}^3}{3}$ and $V_B = \frac{4\pi R_B^3}{3}$, ε_c is given by the Pines and Nozieres expression for the correlation energy discussed in Chapter 2.

Now taking the expressions given by eqns. (10), (12) and (13) together we get E_A^{alloy} as a function of r_{st}

$$E_A^{alloy} = TP1 + TC1 + TK + TX + TC \qquad (14)$$

Now subtracting from it the ground state energy per atom of solute obtained from the uniform density ground state energy discussed in the earlier section of this chapter

the heat of solution of the alloy per atom of A which can be minimised with respect to r_{st}. Here one should note that the matrix electron density is taken to be the same as that of the pure case.

The assumption that as $r \to \infty$, $n(\vec{r}) \to n_B^o$, i.e. the bulk density of the matrix B remains the same as in the pure B, needs to be examined. If it is not so and $\underset{r}{Lim}\, n(r) = n_B^m$ then. $\Delta n = n_B^m - n_B^o$ will be proportional to the concentration c of the solute in the alloy (from the charge neutrality). The atomic radius of the solvent in the alloy will also change (since each WS cell is neutral) leading to an increase in energy proportional to Δn^2 i.e. c^2. But since the size of WS cell to which the solute has to fit in the alloy has changed, there will be an accompanying change in energy proportional to Δn, i.e. c but this change will take place at c-centres of solute making the change in this

energy term proportional to c^2. Hence the total change in energy will be decided by a balance between these two terms and will be proportional to c^2 and so in the dilute alloy limit one can see that since $c \rightarrow 0$ and so $\triangle n \rightarrow 0$ and the assumption that $\lim\limits_{r \rightarrow \infty} n(\vec{r}) = n_B^O$ is quite valid.

Now one can argue that the neglect of δn_B^O i.e. assuming uniform charge density of the matrix, may be quite serious because the effect of alloying will also result in modifying δn_B^O leading to an energy effect. To estimate this energy change we examine the equation (1.31) which shows that the energy effect will be of . second order in the change of δn_B^O. Since the change in δn_B^O due to alloying will be quite small (excepting at the nearest neighbor sites which is taken care of by the construction of $n_{1o}(\vec{r})$ this energy change can be neglected. But if the concentration is high these arguments become invalid.

3.3 The Continuous Model

The step model suffers from a serious handicap since it totally neglects the gradient term in the density functional expansion. This term is by no means negligible and cannot be taken care of by a slight modification of density as has been done by Hodges and Stott[3] (described in Chapter 1). On

the other hand the step model allows for a transparent physical picture leading to separation of the size factor and the electro-chemical contribution in the alloys.

To choose a parametric function for the purpose of modelling the charge density distribution in an alloy we looked into the choice of Smith[20] to model the charge density at the metal surfaces. Smith's form is exponential, i.e. it is given by

$$n(Z) = n_+ - \frac{n_+}{2} e^{\beta Z} \quad \text{for} \quad Z < 0 \text{ (in metal)}$$

$$= \frac{n_+}{2} e^{-\beta Z} \quad \quad \text{for} \quad Z > 0 \text{ (outside)} \quad \quad (15)$$

where n_+ is determined by charge conservation and β is the free parameter to be determined variationally. The resulting charge distribution for different metals is very similar to a tangent hyperbolic function. The calculation of Lang and Kohn[6] with a jellium model for the metal-surface also yields a charge distribution in agreement with the form obtained by Smith. In addition, the later calculation produced small Friedel oscillations in charge density for $Z < 0$ superimposed over the tangent hyperbolic kind of distribution. In the studies of Robinson and de-Chatel[37] also one finds a similar charge distribution for the jellium model Kohn-Sham calculation in heterovalent alloys. From all these

earlier calculations it is obvious that a choice of tangent-hyperbolic functions is quite realistic for our purpose.

So in this model the choice of $\delta n_{AB}(\vec{r})$ is no longer a step but a continuous tangent-hyperbolic function and the electron density of the alloy system can be written as

$$n(\vec{r}) = n_B^O + B[1-\tanh \beta(r-r_o)] + \sum_{l \neq 0} \delta n_B^O(\vec{r}-\vec{R}_l) \tag{16}$$

$$= n_B(\vec{r}) + n_{loc}(\vec{r})$$

$$n_B(\vec{r}) = n_B^O - n_B^O \Theta(R_B - |\vec{r}|) + \sum_{l \neq 0} \delta n_B^O(\vec{r}-\vec{R}_l) \tag{17}$$

and $n_{loc}(\vec{r}) = n_o \Theta(r_{BB} - |\vec{r}|) + B[1-\tanh \beta(\vec{r}-r_o)]$ \hfill (18)

B is a constant determined by conservation of charge, β gives the slope and r_o the point of inflection of this distribution. The last two parameters, β and r_o, are the variables with respect to which the ground state energy is minimised.

Using the expression for $n_{loc}(\vec{r})$ given by eqn. (18) we can evaluate $\Delta \bar{H}_A$ from eqn. (2.49). Here, the two centre terms are no longer zero although in their evaluation also the contribution of $\delta n_B^O(\vec{r})$ has been neglected because it is quite small.

3.3.4 Details of Computation :

For a given β and r_o we can find out B numerically from the charge conservation criterion yielding

$$B = \frac{Z_A - Z_B}{\int [1-\tanh \beta(r-r_0)] \, d\vec{r}} \tag{19}$$

The evaluation of B completely defines $n(\vec{r})$ and hence $n_{loc}(\vec{r})$ and $n_B(\vec{r})$. The integration involved in eqn. (19) has to be done extremely accurately otherwise incomplete cancellation of long range terms in density functional formalism will give rise to residual long range interaction giving rise to spurious results. In our calculation after determining B we have integrated $n_{loc}(\vec{r})$ in the whole space and found it equal to Z_A with an accuracy of $\pm.0001$. To achieve this the above integral has been evaluated analytically from r_0 to ∞ and numerically from 0 to r_0 by 15-point Gaussion quadrature formula.

Now with the $n_{loc}(\vec{r})$ and $n(\vec{r})$ obtained by the above procedure we proceed to evaluate all the integrals involved in eqn. (2.42) again by 15-point Gaussian quadrature formula which we found accurate enough for our purpose by comparing it with the results of higher point quadrature formulas. The two centre integrals involved in eqn. (2.42) have been simplified analytically as given in Chapter 2 leading to eqn. (2.49) and then these are converted into one centre integrals with the help of Lowdin's α-function expansion.

The $\angle H_A(\beta, r_0)$ thus evaluated is minimised with the help of Powel's method of unconstrained minimisation with two variables.

To check the accuracy of the numerical procedures involved we took a $n(\vec{r})$ corresponding to the step model in this scheme and evaluated the energy and compared the results with the analytical results of the step model. The agreement is excellent upto the fourth decimal place giving us the necessary confidence in our computer program and the numerical methods followed.

Chapter 4
Parametric Variational Results and Discussion

In this chapter we present the results of our calculation with the parametric variational scheme described in the last chapter. Both the pure metal and alloy ground state energy have been evaluated to determine the properties of physical interest.

In Section 1 we present the general scheme of investigation we have adopted to achieve our primary aim to investigate the systematic trends in alloying behaviour. This will familiarise the reader with the fact that our purpose of the studies on pure metals emerges from the necessity of the studies on alloys.

In Section 2 we present the cohesive energy, equilibrium atomic radius and the charge density for elements with different core radii in both the uniform gas model and the cosine model in the density functional formalism. We have also presented here our results on the estimate of the contribution to the cohesive energy of the periodic component of charge density in the linear response theory to compare it with density functional results.

In Section 3 we present the heat of solution of the alloys broadly under two categories (i) fixed matrix and the varying impurity and (ii) the fixed impurity and the

varying matrix. Then an attempt has been made to compare
the calculated results with the experimental results.

In this section we also examine the prevalent ideas
on the effect of size factor and electrochemical factor
in alloys. The discussion of the latter effect necessitated
a brief discussion on chemical potential.

In Section 4 we discuss our failures in the case of
alloys with solutes of higher valency compared with the
valency of the matrix. Our further attempts to form alloys
with the solute having the ground state charge density given
by the cosine model are described.

4.1 Scheme of this Investigation

In the Ashcroft empty core model potential any ele-
ment of a given valency can be characterised by its core
radius. Although this core radius is an artifact of the
model having no rigorous physical standing, it is generally
identified with the ionic radius of the elements. This
can be understood in view of the cancellation theorem, i.e.
within the span of this ionic radius the core state wave
functions exist and, due to their orthogonality to the
valence state, cancels the effect of the ionic potential
within this radius. If one calculates the r_s, the radius
of the sphere containing one electron in the element, from

the minimal property of the ground state energy by a uniform
electron gas model one gets an approximately linear curve.
This linearity remains intact even after assuming a linear
response screening excepting for very low value of the core
radius. So, in general one can take a systematic variation
of r_c to be equivalent to a regular variation of r_s. Now the
atomic radius being directly proportional to the r_s for a
given valency, r_c becomes a measure of the atomic size of the
elements. For the same valency r_c is a measure of the
strength of the potential also. Hence a systematic variation
of r_c is equivalent to a variation of the strength of the ionic
potentials as well as the charge density for the same system
of electron gas as we go along a homovalent series. Inciden-
tally, Inglesfield has taken the difference in the depth of
the pseudopotentials in homovalent binary alloys as a
measure of difference in electronegativity. So by varying
this parameter r_c we are able to systematically study the
effect of size-difference and electrochemical factors in
alloys as it will be detailed in later sections.

Eqn. (3.2) of the last section expresses the ground
state energy E_g as a function of R_0 which in turn is pro-
portional to r_s for a given valency. This E_g will also be
a function of r_c which is characteristic of an element

and hence for a given r_c we can minimise E_g with respect to r_s to get the r_c vs rs curve for a given valency. Singh and Young have already calculated such a curve including the contribution of the periodic components of density in linear response theory. We also calculate the same results essentially to check the accuracy of our numerical procedure. But we use Nozieres-Pines expression for the correlation energy and Hubbard-Sham dielectric function in place of the Hartree dielectric function. Our results agree in general with that of Singh and Young including the non-linear nature of this r_c-r_s curve at low r_c as shown in Fig. 4.1. Since our model for the alloy completely neglects the periodic component we minimise the eqn. (3.2) i.e. the energy of a sphere of electron gas of uniform density and obtain the r_c vs r_s curve as shown in Fig. 4.2. This curve is almost linear providing a good basis for the study of alloying behaviour along these curves.

The non-linearity in Fig. 4.1 probably indicates that for such low value of r_c /the pseudopotential becomes strong enough to make its treatment by second order perturbation theory invalid. Otherwise the general trend of both Figs. 4.1 and 4.2 are quite understandable in the sense that for the same r_c the higher the valency, the lower is the r_s;
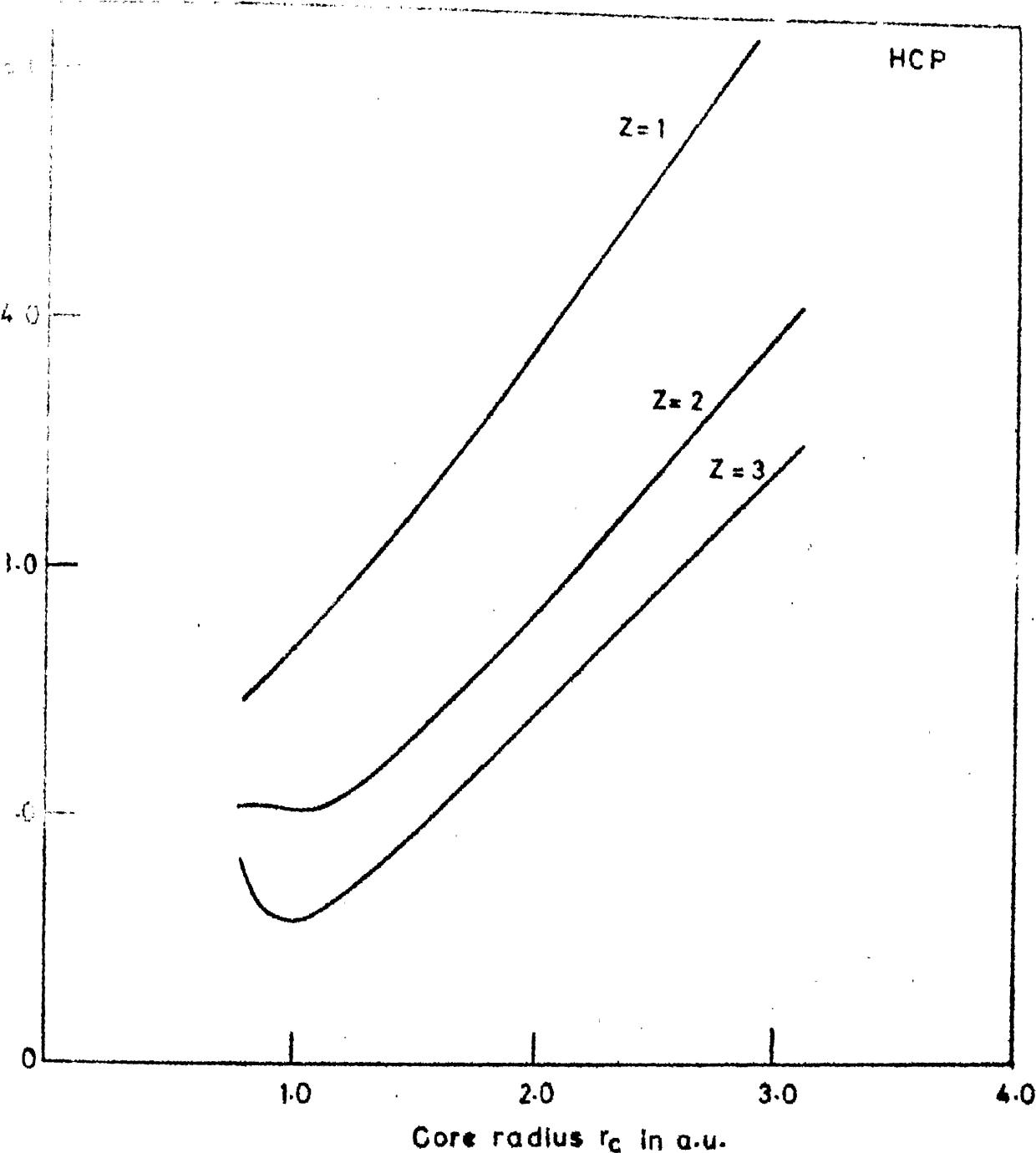
FIG 4.1 : VARIATION OF r_s WITH CORE RADIUS (r_c) FOR HCP STRUCTURE IN LINEAR RESPONSE THEORY FOR DIFFERENT VALENCIES (a) Z = 1.0 (b) Z = 2.0 AND (c) Z = 3.0.
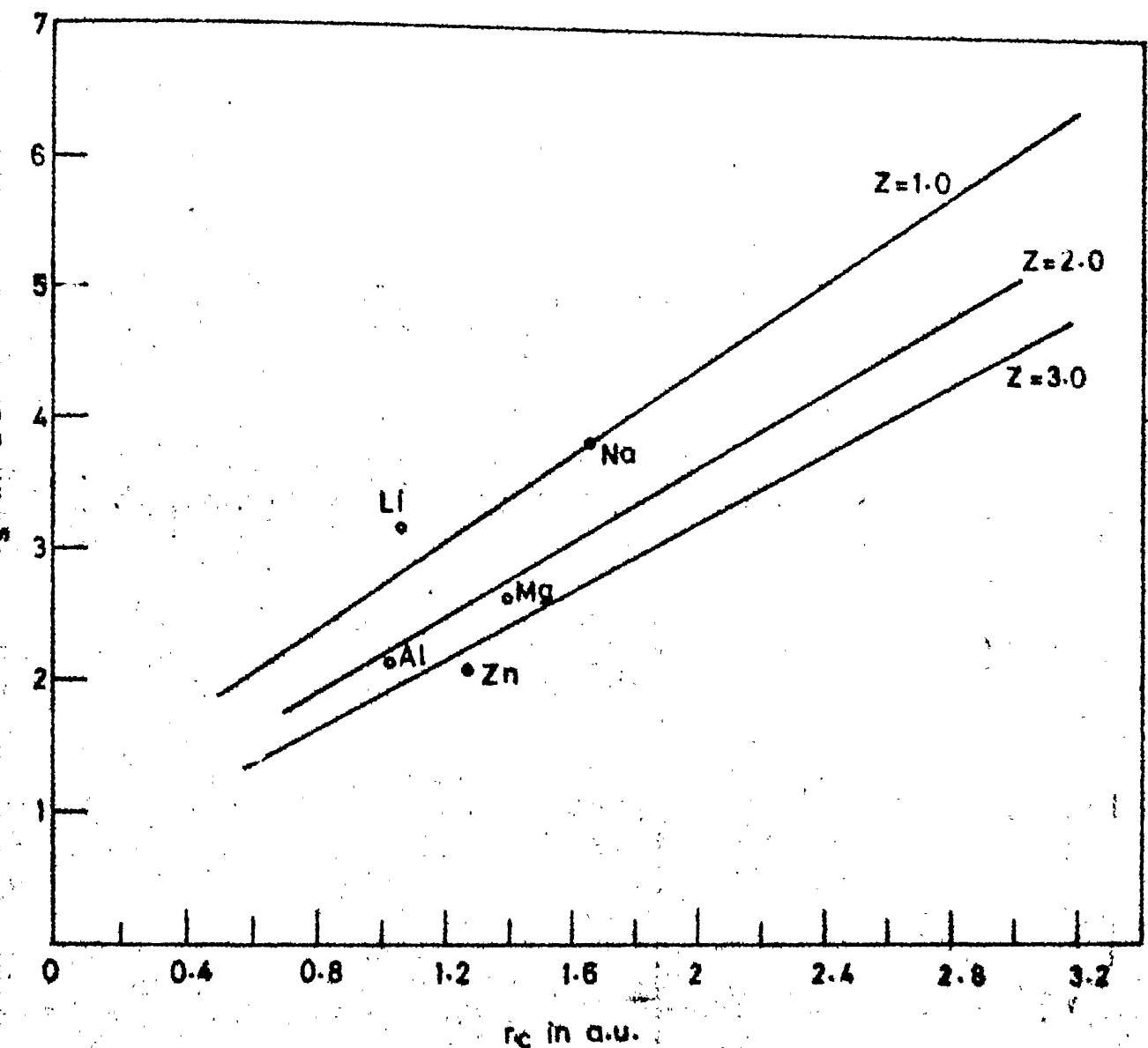
FIG 4.2 : VARIATION OF r_s WITH CORE RADIUS (r_c) IN THE UNIFORM
ELECTRON GAS MODEL FOR DIFFERENT VALENCES : (a) Z = 1.0
(b) Z = 2.0 AND (c) Z = 3.0 •— EXPERIMENTAL RESULTS.

because higher valency gives stronger potential to pull the electrons towards the ions and hence results in higher density of electrons i.e. lower r_s.

One should note that these results given in Fig. 4.2 differ from that of Ashcroft and Langreth[39] although the agreement of cohesive energy for a given r_s and valency is better here as it will be discussed in the next section.

4.2 Cohesive Energy of Pure Metals

As described in Chapter 3, the cohesive energy in pure metals has been studied in two different models (a) uniform electron gas model (b) the cosine density model. The motivation for taking resort to the latter model is also described. Here we will present the results obtained in these two models in the following two sub-sections.

(a) Uniform electron gas model :

To give an idea of the nature of variation of the energy in this model with respect to r_s we present in Fig. 4.3 a sample of our calculation for $Z = 2.0$ and $r_c = 1.0, 1.7$ respectively. Also we show the contribution of the periodic variation of density in the linear response theory. The curves denoted by U represent the structure independent energy or the energy in the pure uniform electron gas model.
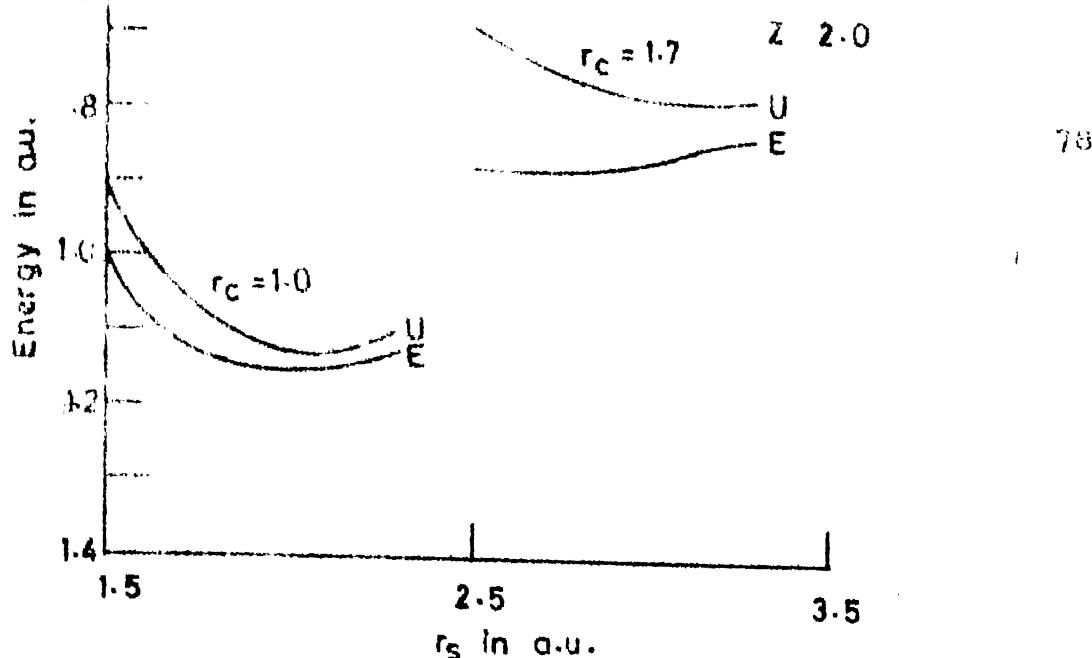
FIG 4.3 : VARIATION OF ENERGY WITH r_s, U-UNIFORM ELECTRON GAS MODEL, E-LINEAR RESPONSE THEORY FOR DIFFERENT VALENCIES (a) Z = 1.0 (b) Z = 2.0 AND (c) Z = 3.0.
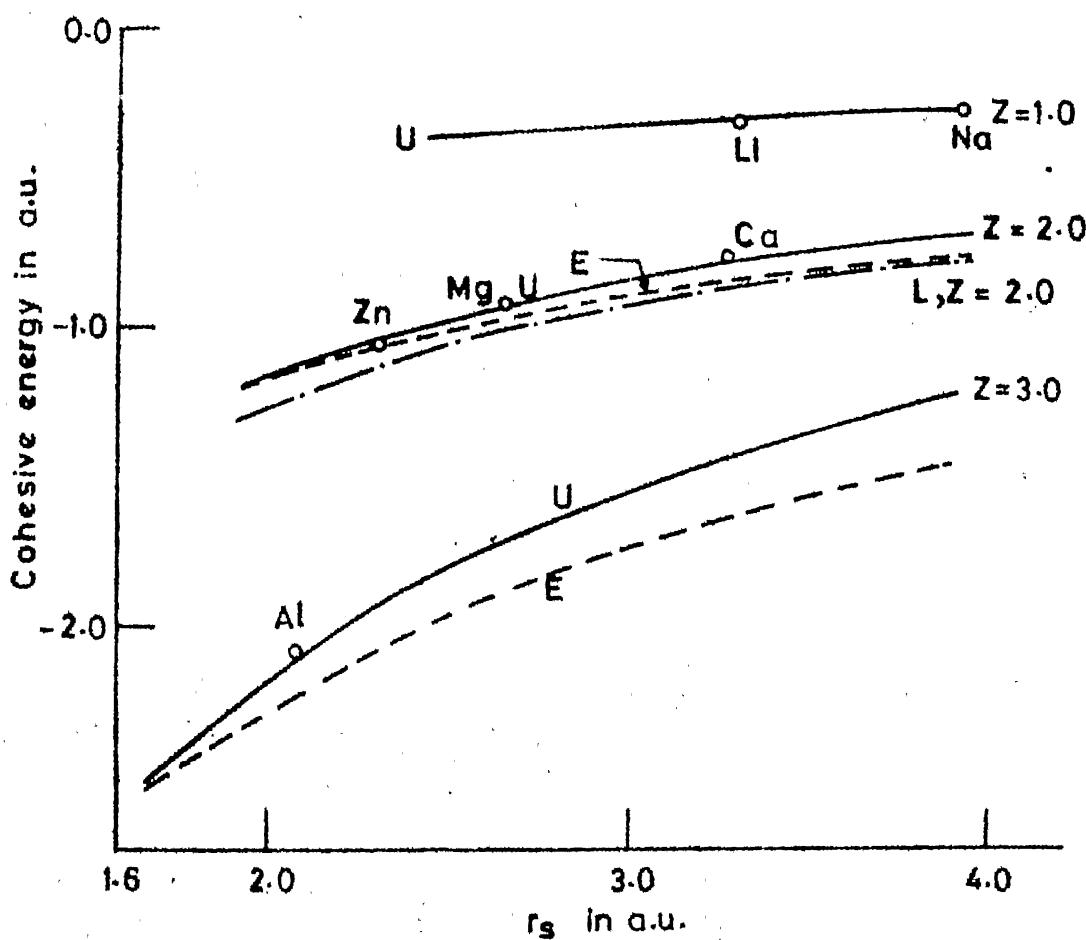
FIG 4.4 : VARIATION OF COHESIVE ENERGY WITH r_s: (i) U-UNIFORM ELECTRON GAS MODEL, (ii) ----- LINEAR RESPONSE THEORY FOR DIFFERENT VALENCIES -------- WITH CORRELATION ENERGY GIVEN BY GUNNARSON ET AL: (a) Z = 1.0, (b) = 2.0, and (c) Z = 3.0.

Fig. 4.4 shows the variation of cohesive energy i.e. the position of the minimum of Fig. 4.3, with respect to r_s for the uniform gas model by the firm lines for different valencies. The observed value of r_s and cohesive energy of some of the simple metals are also shown in this figure by circled dots for a comparison with the calculated curve. For $Z = 1.0$ we could not show the contribution of the periodic variation of density because it is so small that it can not be shown separately in this scale of the figure 4.4.

There are several expressions available for the correlation energy of the uniform electron gas. We have used the expression given by Nozieres and Pines (in atomic units) as

$$U_o \simeq -0.0575 + 0.0155 \ln r_s$$

per electron. We also tried to use the interpolation formula used by Gunnarson[29] et al and the results for $Z = 2.0$ are plotted in this Fig. 4.4 as the dash-dotted curve marked by L. This curve shows similar results as the NP exchange but the agreement with the observed cohesive energy is inferior in this case. So we abandon this interpolation formula and use the one given by Nozieres and Pines consistently throughout this study.

The agreement of the observed values of cohesive energy and r_s with the calculated curve is quite excellent compared to the previous works of Ashcroft[38] et al and that of D. Wearie[39]. The former study did not achieve such good agreement in cohesive energy whereas the latter study starting with the Animalu-Heine Model potential for different elements, did not get good agreement with the observed r_s values.

For the purpose of our study if we define the core-radius r_c of an element as the one which corresponds to the observed atomic radius in the uniform electron gas model, we find a disagreement with the core radii derived from the observed resistivity or the fermi-surface data. This is expected on two counts: (i) due to ignoring the periodic contribution which has been taken care of within the framework of the second order perturbation theory while deriving the core radii from the FS or resistivity data (ii) due to the fact that FS or resistivity data reflects the effect of the ionic potential on the states near the FS and so will simulate the scattering of the electrons in these states only, whereas the core radii found out on the basis of cohesive energy will give a better model potential when the scattering of all the electronic states in a band from the ionic potential is important.

If we define r_c as indicated above then our calculation yields a much better agreement with the observed value of E_g (corresponding to an atomic radius) than any other previous study.

(b) The Periodic Density Variation :

The uniform charge density model, although is well known to account for most of the cohesive energy ($\sim$ 90-95 percent by earlier accounts, our result shows it to be even higher) but still a small contribution from the periodic component of density is observed. Since we are interested finally in the heat of solution of the alloys which are quite small (in cases nearly of the order of the cohesive energy contribution of the periodic component) it is desirable at least to understand this contribution if not accomodate it in our study of the alloy. Customarily, this has been studied under the linear response theory but we find it quite unreliable in the limits when of small r_c and large r_o coupled with the empty core model pseudopotential. So, we study the ground state energy with the formalism of the density variational method along with the gradient term as described in Chapter 2.

(i) The results of the linear response theory :

The curves denoted by B in Fig. 4.3 show the variation

of Energy with r_s including the contribution of the periodic variation of density for $Z = 2.0$ and the core radii $r_c = 1.0$ and 1.7 for fcc structure. The calculation for the h$\bullet$p structure shows almost the same values of E for a given r_s. It is expected because the energy involved in allotropic change between these two structures are observed to be extremely small if the volume per atom remains the same. The behaviour of these E vs r_s curves shows that as r_c becomes larger the total energy for a given r_s is higher because the attractive ionic potential becomes weak. Also for a given Z as r_c increases the energy contribution of the periodic component of the charge density increases. When the core radius is large, only by piling up electrons in the attrative region outside the core can the systems reduce its energy giving rise to a ground state density with strong spatial dependence i.e. periodic component is large. This is observed as a systematic trend in Fig. 4.4. Here the dotted lines give: the energy including the periodic density contribution at the r_s obtained by minimising the energy of the uniform density electron gas. This procedure is justifiable on the ground that the periodic density contribution is extremely small compared to that of the uniform component But for high r_c the periodic contribution increases significantly and the above procedure may not hold. This increase in the

periodic contribution with r_c may, however, be an artifact
of the empty core pseudopotential.

This periodic contribution increases with valency also,
as expected, because the periodic potential gets stronger
with Z. But when Z is large the potential may be strong
enough to the extent that the linear response theory if
applied may overestimate the periodic contribution.

In general, it appears that the linear response theory
coupled with the Ashcroft empty core pseudopotential tends to
exaggerate the periodic contribution increasingly
with increasing r_c and for the low r_c and high valency it
gives a wrong estimate (Fig. 4.1).

From Fig. 4.3 one can also see that the rate of variation
of this periodic contribution with r_s can dominate over the
rate of variation of the structure independent uniform ele-
ctron gas energy with r_s, for higher r_c's and as a result
one can find an r_s corresponding to the minimum in total
energy quite different from that corresponding to the minimum
of the uniform electron gas energy. Since for the reasons
mentioned in the above paragraph, we suspect the estimate of
the periodic contribution under the model of empty core poten-
tial, we took the model of uniform electron gas without the
periodic variation of density to depict the electron

distribution of pure metals in the context of alloys. For-
tunately also it gives quite a good agreement with the
observed cohesive **ener**gies justifying to an extent this
model. This model does lead to /difficulty in the cases of alloys
with impurities of higher valence which will be discussed
in the appropriate place. As a result it becomes important
to deviate from this model for pure metals in an effort to
find a satisfactory treatment of the above alloys. In the
next section we incorporate a periodic variation in density
and evaluate the cohesive energy of pure metals by the
density functional formalism in place of linear response
theory.

(ii) The Density Functional Results :

In this scheme we use a density distribution of the
form $n_0 + B \cos kr$ with three parameters n_0, B and k as
described in the last chapter. n_0 is determined by charge
conservation and the other two parameters are determined
variationally using the minimal property of the ground state
energy. The numerical scheme is similar to that of the
tangent hyperbolic density model of the alloy. In this
scheme we find out the dominating contribution from the set
of k's which obviously will be the one having half the
wavelength within the atomic radius. Other smaller wavelengths

will have larger gradient term contribution reducing their effect on cohesive energy. This dominating k is related to atomic radius R . by

$$R = \pi/R \cdot R \quad (=\pi/k) \quad \text{and} \quad B \quad \text{are determined by minimum}$$
$$E_g.$$

Fig. 4.5 shows a plot of R . as determined by this method for valencies Z = 1.0, 2.0 and 3.0 respectively. From this figure we can see that at core radius (r_c) greater than 2.1 this R_{at} vs r_c curves deviate from the linearity observed for lower values of r_c. The dotted curve at the top shows the r_c vs R . curve of the uniform electron gas model for valency Z = 3.0. The comparison of the dotted curve with the Z = 3.0 curve for the model shows that the relative deviation of R increases with increasing r_c (1.5 percent at r_c=0.8 and 17/ percent at r_c=2.7 This may be explained in terms of the periodic effect we see for the empty core potential. But this deviation is quite small with low r_c and increases with the increase in valency.

Figure 4.6 shows the difference ΔE in cohesive energy between the uniform gas model and the cosine model as a function of r_c. We see that there is a general increase in the periodic contribution ΔE with increasing r_c. This can be understood in view of our argument that if r_c is large electrons have to pile up in the small attractive
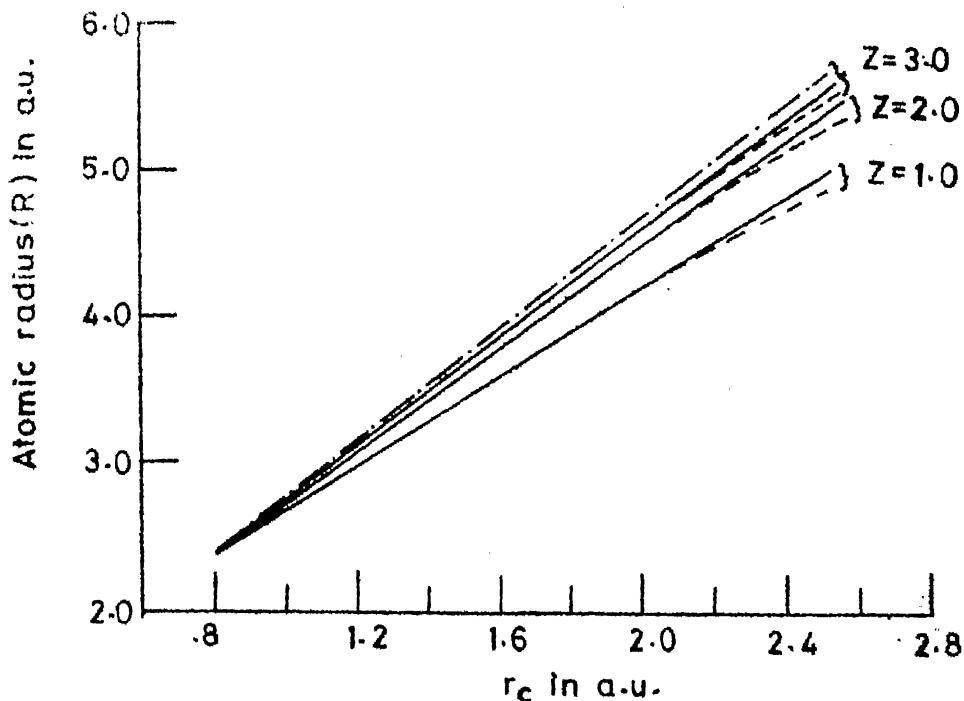
FIG 4.5 : VARIATION OF EQUILLIBRIUM ATOMIC RADIUS (R) WITH
CORE RADIUS (r_0) IN THE COSINE MODEL FOR VALENCIES
(a) Z = 1.0, (b) Z = 2.0 AND (c) Z = 3.0, (d) ———
FOR UNIFORM ELECTRON GAS MODEL Z = 3.0.
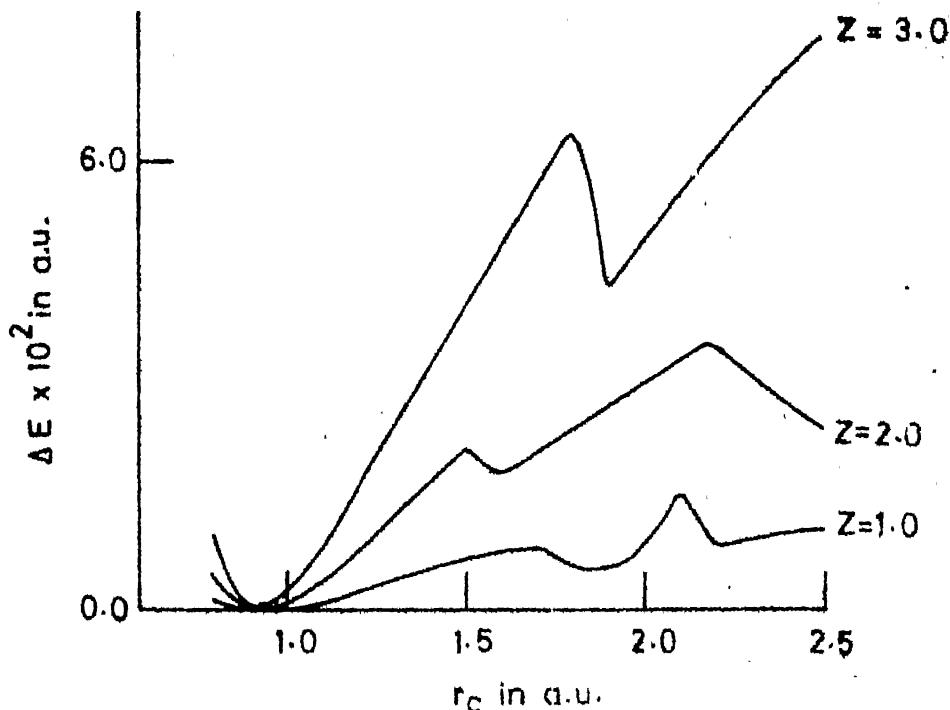
FIG 4.6 : VARIATION OF DIFFERENCE IN GROUND STATE ENERGIES
(ΔE) WITH CORE RADIUS (r_0) BETWEEN THE COSINE
MODEL AND THE UNIFORM ELECTRON GAS MODEL FOR
(a) Z = 1.0, (b) Z = 2.0 AND (c) Z = 3.0.

region $r_c < r_o < R$, and hence the periodic component and
its contribution to the cohesive energy increase Fig. 4.7
shows the variation of ΔE with the valency Z. ΔE increases
almost as Z^2 for $r_c = 1.7$. If we examine in the same
figure the variation of $-n_o/B$ with Z we find that it satura-
tes at high Z($>$ 3.0), i.e. with Z = 3.0 and beyond   B
increases in proportion to n_o. Fig. 4.8 shows the variation
of $-n_o/B$ | with r_c for different Z, starting from $r_c = 1.2$.
We find that with increasing r_c the   periodic component
|B| increases faster than n_o (i.e.|B|/n_o increases until it
reaches a certain value then again |B|/n_o decreases
(probably discontinuously). This is not expected, since the
g.s.e. E_g is a smooth function of r_c, B, and R. Most likely
this effect is due to an incomplete search for the true
minimum, i.e. the minimum obtained may be a relative minimum
but not the absolute or global   minimum. We have not
pursued this further since the energy differences are small,
and the values obtained here (beyond the jump) are not used
in further computations. For small r_c = 0.8, 0.9 we find
that B is positive indicating a pile up of charge at the
centre. This is because the strongly attractive region of
the potential is too near the core leading to a pile up of
charge there and this continues even inside the core because
gradient term does not allow the charge density to fall
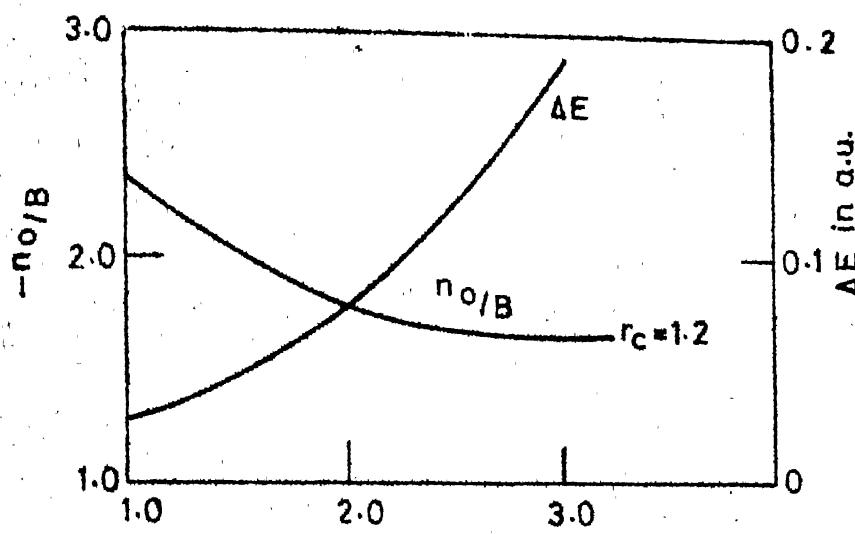
FIG 4.7 : VARIATION WITH VALENCY, Z, OF (a) DIFFERENCE IN GROUND
STATE ENERGIES (ΔE) BETWEEN COSINE MODEL AND UNIFORM
ELECTRON GAS MODEL (b) RATIO OF UNIFORM TO PERIODIC
COMPONENT OF DENSITY (n_0/B) IN COSINE MODEL.
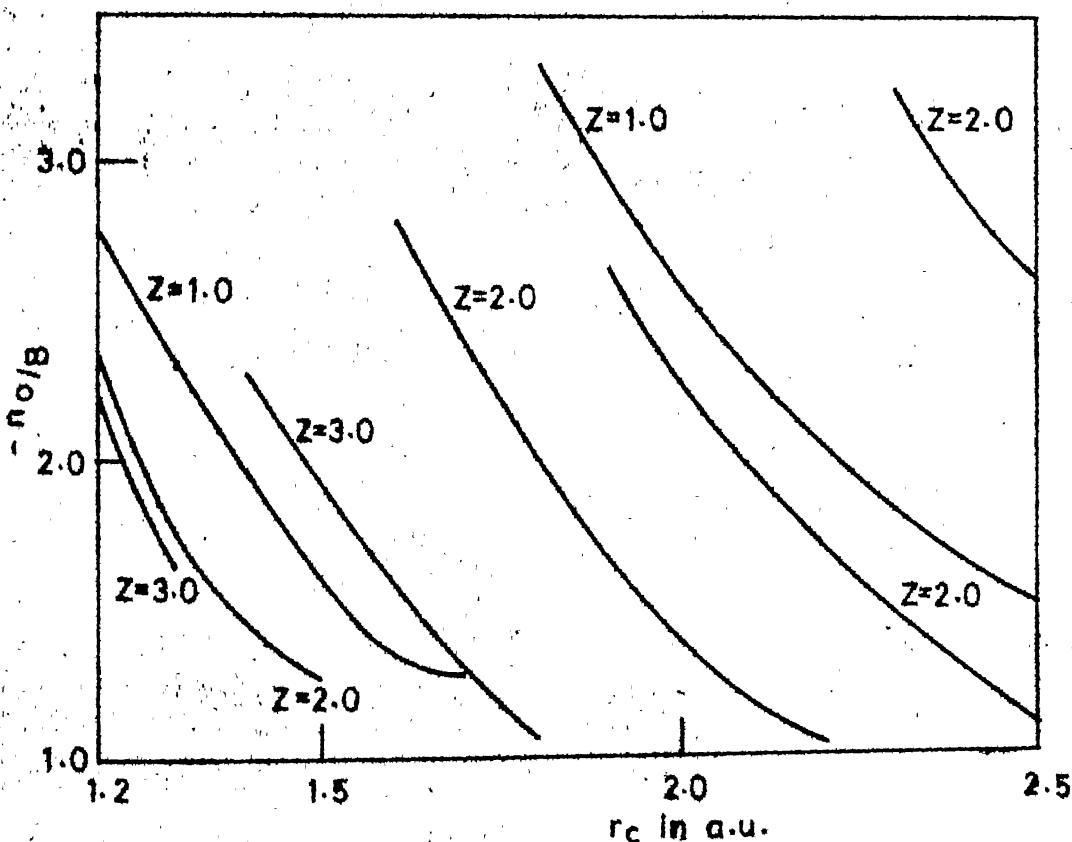
FIG 4.8 : VARIATION OF RATIO OF UNIFORM TO PERIODIC COMPONENT
OF DENSITY (n_0/B) WITH CORE RADIUS (r_c) IN COSINE
MODEL FOR DIFFERENT VALENCIES (a) Z = 1.0, (b)
Z = 2.0 AND (c) Z = 3.0.

sharply. The cosine form of charge density may not have correctly represented the density in this case.

If one compares the periodic contribution to the cohesive energy from the cosine model and that from the linear response theory one can easily see the tendency of linear response theory to overestimate the periodic contribution to E_g in general. For low $r_c (= 0.8$ or $0.9)$ we find (n_0/B) positive and large indicating a small pile up of charge at the core region. The linear response results in this region shows a deviation from its normal behaviour as shown in Fig. 4.1 and since the potential is quite strong for low r_c these results are suspect.

4.3 The Heat of Solution of Alloys in the Parametric Variational Model

The calculations have been done on the following systems: fixed matrix with varying alloy element, and fixed alloy element with varying matrix. By fixed, we mean that the valency Z is fixed as well as the core radius r_c (and thus the atomic size). By varying, we mean that for a given Z, the core radius r_c is varied. Thus one is able to study for a given valence difference, the effect of size difference (e.g. difference between the equilibrium atomic radii R_A and R_B) as well as the effect of the chemical potential or

electro-negativity difference. The latter depends on the electron density which varies smoothly with r_c. Such a set of calculations should bring out clearly any systematic trends in the alloying energies etc. The observed heats of solution for different alloys correspond to the heats of solution for particular values of r_c's for a given $Z_A - Z_B$ combination. Even though the actual values of the heat of solution may not agree well with experiment, the trends observed may have deeper validity to be confirmed by experiments, symbolically, the matrix-impurity combination can be represented as $MZ_B - IZ_A$. The former set (fixed matrix varying impurity) contains results for the following: $Z_B = 3$ and $Z_A = 1,2$ $Z_B = 2$ and $Z_A = 1,3$ and $Z_B = 1$ and $Z_A = 2$ and 3. In the latter set (fixed impurity varying matrix) we have the results for $Z_B = 2$ and $Z_A = 1$.

The results can clearly be classified according to the relative valencies of the matrix and the impurity, i.e. $Z_B > Z_A$, $Z_B = Z_A$ and $Z_B < Z_A$. The variational parameters we have used to describe $n(\vec{r})$ are such that only in the last case can we study the alloying effect. The reason is as follows. In the case $Z_B > Z_A$, we generally find no charge transfer, but only a redistribution of $n(\vec{r})$ within the WS cell corresponding to the impurity. That is, in the step model the step occurs at $r_{st} < R_B$, and in the tanh model

(a)

(b)

(c)
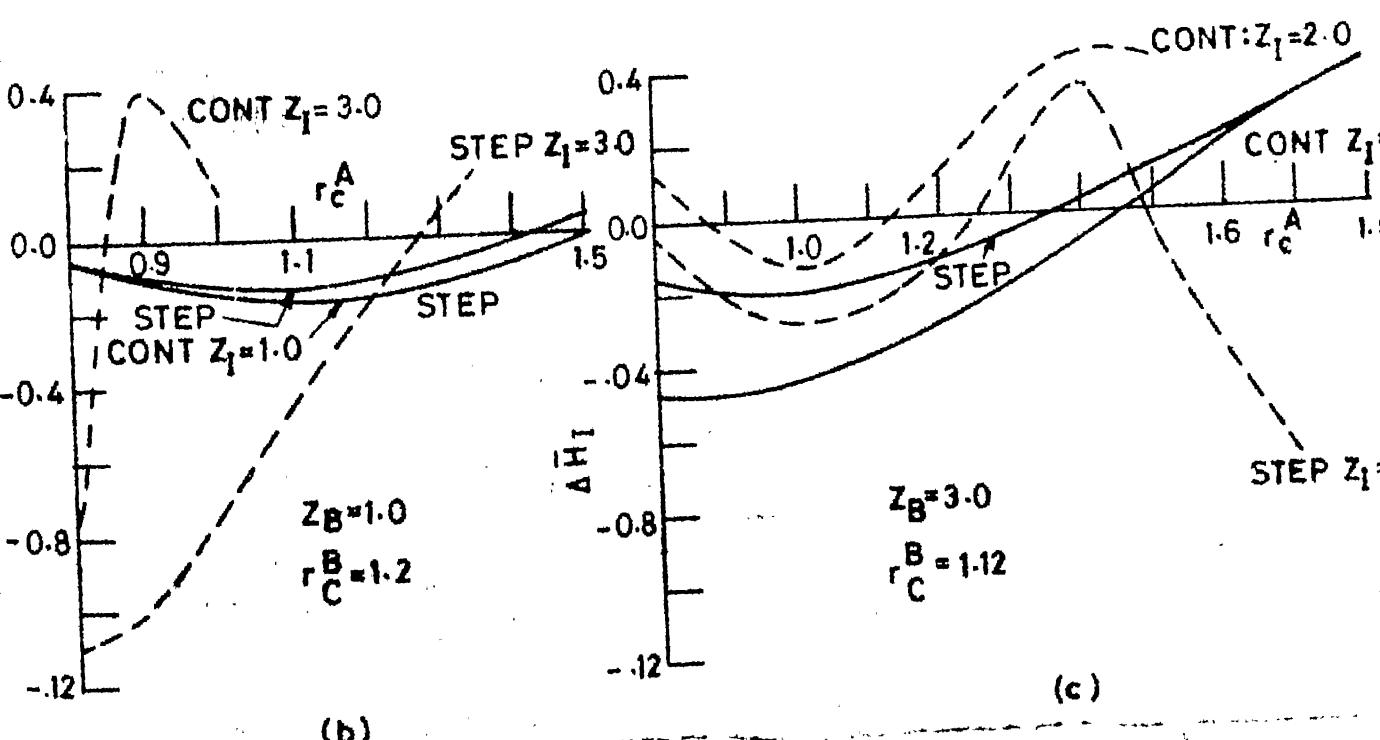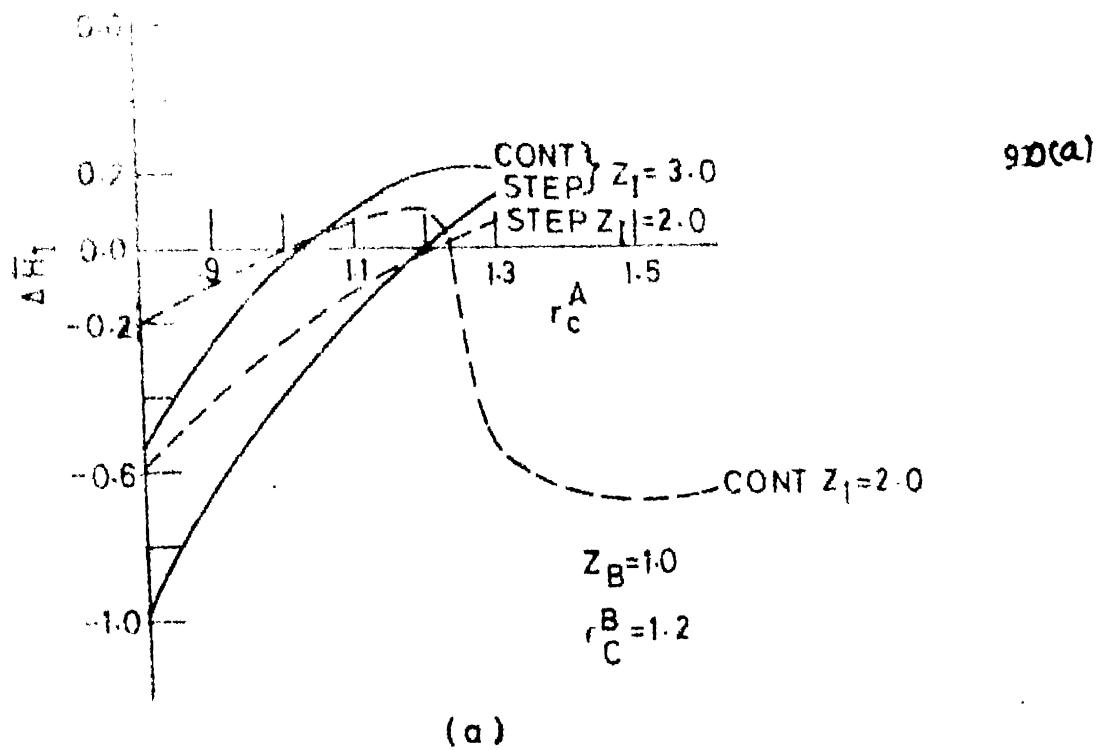
FIG 4.9 : VARIATION OF HEAT OF SOLUTION, $\Delta \bar{H}_I$, WITH CORE RADIUS OF SOLUTE ($r_c{}^A$) FOR SOLVENT WITH VALENCIES (a) $Z_B=1.0$ (b) $Z_B=2.0$ AND (c) $Z_B=3.0$. STEP: STEP MODEL; CONT: CONTINUOUS MODEL.

for $n(\vec{r})$ the turnover point $r_o < R_B$. This modification of
the ground state profile might be due to the host environ-
ment, or it might be intrinsic, i.e. present in the pure
metal A as shown in Section 4.2. Because of the lack of charge
transfer, this does not fall into the canonical alloying
scheme, we however, discuss the results for this case in a
lattor section in some detail. In the case $Z_B = Z_A$, it can
be shown, that one can have no step in $n(\vec{r})$ nor can one have
an additional tanh kind of distribution. This follows
simply from charge neutrality. In our variational parametri-
zation, scheme the only contribution to $\Delta \bar{H}_I$ is due to di-
fference in atomic volumes. Clearly, a more sophisticated
density profile is needed for the homovalent case.

We thus turn to the case $Z_B < Z_A$, where we find charge
transfer and thus alloying in the conventional sense. We
present our result as follows :

(a) Fixed matrix with varying alloy elements :

Figs. 4.9(a), (b) and (c) present respectively the
results for the matrices with valencies Z_B = 1.0, 2.0
and 3.0, the core radii in these three cases have been
r_c^B = 1.12, 1.2 and 1.2. Apparently these curves represent
widely varying trends for different $MZ_B - IZ_A$ combination.

But in most of the cases the results of the step model
follows the general trend of the results of the continuous
tangent hyperbolic model although quantitatively the
results of these two models are different. Clearly it
indicates the importance of the contribution of the gra-
dient terms in alloying. The values of r_0 and r_{st} are also
different because the tanh model does not merely relax the
step keeping its turnover point r_0 at $r = r_{st}$ but it shifts
the turnover point also from $r = r_{st}$ to $r_0 < r_{st}$ in all the
cases (See Table 4.1). In the M3-I1 and M3-I2 set the heat
of solution of the step model is greater than that evaluated
by the continuous model but for M2-I1 we get the contrary
result'. As we go from the former model to the latter we
find that two opposing tendencies develop: (i) changing the
charge transfer contribution to the energy, i.e. the
negative energy contribution of the surface dipole energy
and (ii) the positive energy contribution from the gradient
terms. As a result the charge distribution $n(\vec{r})$ readjusts
itself to arrive at a new minimum.

The widely varying trends of the heat of solution
$\Delta \bar{H}_I$ Vs the core radius of the solute r_c^A as given in these
figures are due to the fact that for the sets where
$Z_B < Z_A$ there are no electro-chemical interaction between
the solute atom and the matrix because it was found that

TABLE 4.1

The parameters of the ground state charge density in alloys

r_c^A	M1-I2 STEP r_{st}	M1-I2 CONT r_0	M1-I2 β	M1-I3 STEP r_{st}	M1-I3 CONT r_0	M1-I3 β	M2-I1 STEP r_{st}	M2-I1 CONT r_0	M2-I1 β
0.8	1.9	1.93	2.71	2.1	2.00	2.53	3.8	3.60	1.31
0.9	2.1	2.16	2.64	2.3	2.23	2.43	3.8	3.58	1.32
1.0	2.3	2.37	2.52	2.5	2.43	2.30	3.7	3.54	1.35
1.1	2.6	2.60	2.59	2.7	2.62	1.95	3.7	3.50	1.38
1.2	2.8	2.87	.70	3.0	2.82	1.71	3.6	3.46	1.42
1.3	3.2	6.17	.70	3.3	3.14	.70	3.5	3.40	1.46
1.4	–	6.17	.70	–	6.12	.70	3.4	3.34	1.53
1.5		6.17	.70		6.12	.70	3.3	3.26	1.60
1.6							3.1✳	3.19	1.68
1.7							2.5✳		
1.8									
1.9									

– at the end of a column indicate that our computational scheme did not show a minima upto the distance of the next nearest neighbor.

✳ indicates complete drainage of valence electrons from a region with $r < r_{st}$

$r_{st} < R_1$ and so also r_o. This is equivalent to a redis-tribution of charge within the impurity cell which since deviates from its ground state configuration should give an increase in energy. But we find that in such cases also there is a negative region of $\Delta \bar{\bar{H}}_I$ which is puzzling. Our attempt to investigate this problem will be reported at the end of this chapter. If we ignore these results for $Z_B < Z_A$ the rest of the sets (i.e. the results for $Z_B > Z_A$) follows a definite trend which we plot separately in the next figure.

In Fig. 4.10 we show a plot of the atomic radius R_A of the alloying elements VS the heat of solution $\Delta \bar{\bar{H}}_I$ at infinite dilution for these cases where alloying has taken place. It includes three sets of variational results denoted by M3-I1, M3-I2 and M2 - I1. This figure also includes one non-variational result for M3 - I3 for the purpose of comparison.

These results show that as an alloying element with differing lower valency is introduced in a matrix the $\Delta \bar{\bar{H}}_I$ VS R_A curve becomes asymmetric. This clearly is due to the electro-chemical effect because in the alloying with components of same valency the size factor only has got a role to play and leads to a nearly symmetric $\Delta \bar{\bar{H}}_I$ VS
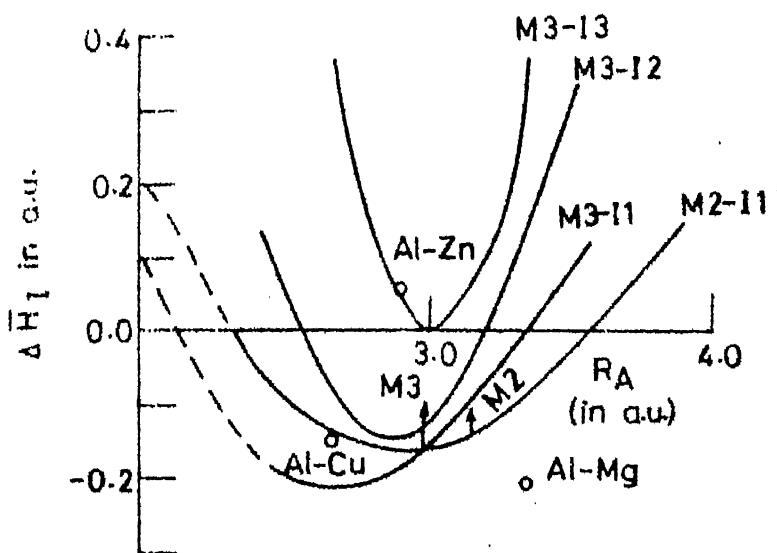
FIG 4.10 : VARIATION OF HEAT OF SOLUTION, $\Delta \overline{H}_I$, WITH SOLUTE ATOMIC RADIUS, R_A, FOR (a) M3 - I3, (b) M3 - I2, (c) M3 - I1 (d) M2 - I1 SYSTEMS. EXPERIMENTAL RESULTS.
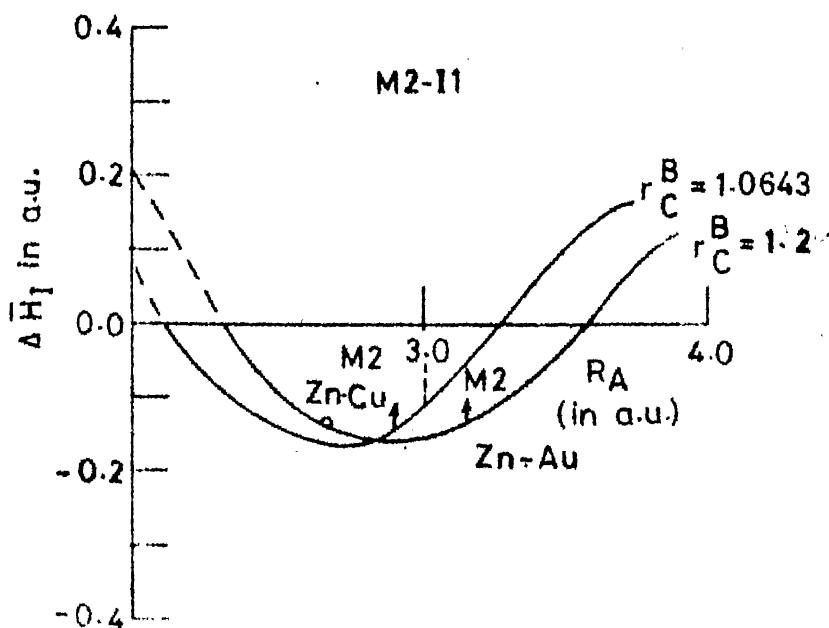
FIG 4.11 : CHANGE OF HEAT OF SOLUTION, $\Delta \overline{H}_I$ V$_S$ SOLUTE ATOMIC RADIUS, R_A CURVE WITH CHANGE OF SOLVENT B RADIUS (a) $r_C^B = 1.0643$, (b) $r_C^B = 1.2$.

R_A curve as given by the M3 - I3 set of Fig. 4.8. But when we go to M3 - I2 or M3 - I1 we find curves for $\triangle \bar{H}_I$ whose assymetry increases with increasing difference of the valencies $\triangle Z$ of the constituents. The minimum of these curves shifts to a lower and lower size away from the atomic size of the matrix with increase in $\triangle Z$. In other words the electro-chemical factor in these cases makes alloying with impurities of the smaller atomic radius ratio (radius ratio $<$ 1) more favourable compared to that of the elements with larger atomic radius ratio (radius ratio $>$ 1) so, the nature of 15 percent rule of Hume-Rothery should incorporate an asymmetry due to electro-chemical factor of the non-homovalent alloys and this limit of 15 percent should increase with the difference in the valencies of the constituents. One notices in Fig. 4.9(c) a drooping of the M3 - I2 and M3 - I1 curves corresponding to the whole charge of lower valence impurity getting stuck to the charge of the matrix leaving an almost charge free region in the centre. This is equivalent to readjustment of charge in the impurity cell and so should lead to a positive energy change contrary to that shown in Fig. 4.9(c) for M3 - I2 for the step model but of course the continuous model rectifies this situation. This particular trend may be an artifact of this potential due to similar reasons as mentioned for the pure case.

Figure 4.11 shows the effect of change of r_c^B (core radius of matrix) on the $\Delta \bar{H}_I$ VS R_A curve. A reduction in results in a reduction of atomic size of the matrix and hence this curve shifts as expected to the lower size. There is no significant change in the depth of the minimum which appears to be a strong function of the difference in valency of the constituents only.

(b) Fixed impurity with varying matrix :

Figure 4.12 shows the $\Delta \bar{H}_I$ VS R_B results for a system with the matrix and the impurity having valencies $Z_B = 2.0$ and $Z_A = 1.0$ respectively, the core-radius of the impurity being $r_c^A = 1.5$. The corresponding R_A is shown by the dotted line in the figure. This curve does not show any new aspect but only confirms the nature of the asymmetry observed earlier. The minimum always lies where $R_A < R_B$ and the alloying with solvents of larger atomic radii is more favourable than that with the solvents of smaller atomic radii.

The maximum calculated negative value of the heat of solution is in the range -0.02 to -0.03 a.u. or 12 to 18 KCal/mole. This is also in the range of maximum observed value. This number is very small in comparison to the cohesive energy (~ 5 percent). Often, observed heats of
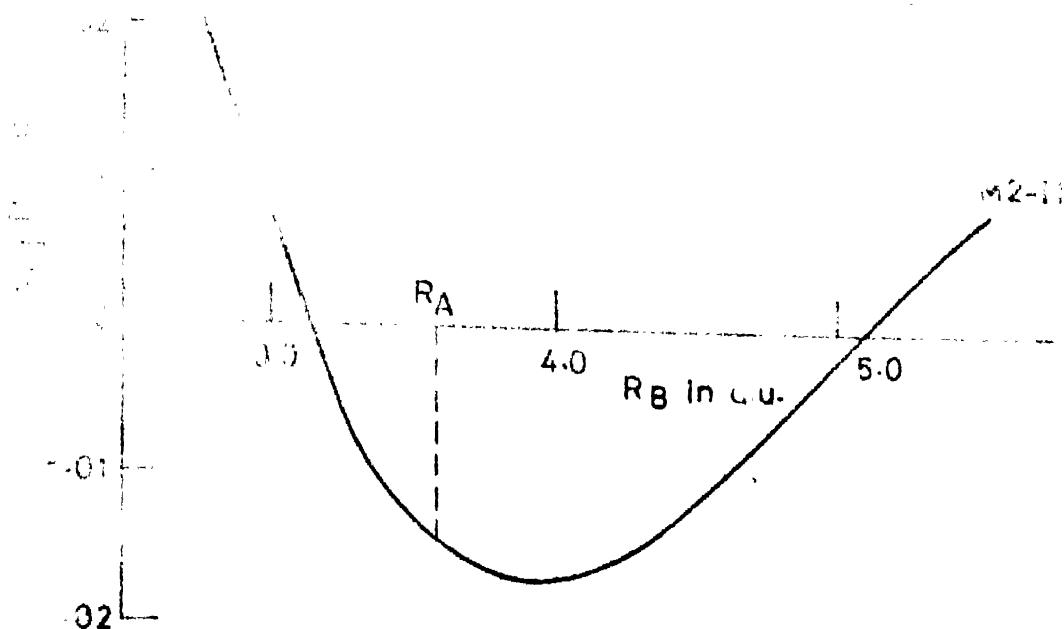
FIG 4.12 : VARIATION OF HEAT OF SOLUTION, $\Delta \bar{H}_I$, IN CONTINUOUS
MODEL WITH SOLVENT ATOMIC RADIUS, R_B FOR SOLUTE WITH
FIXED ATOMIC RADIUS, R_A, IN M2-I1 SYSTEM.
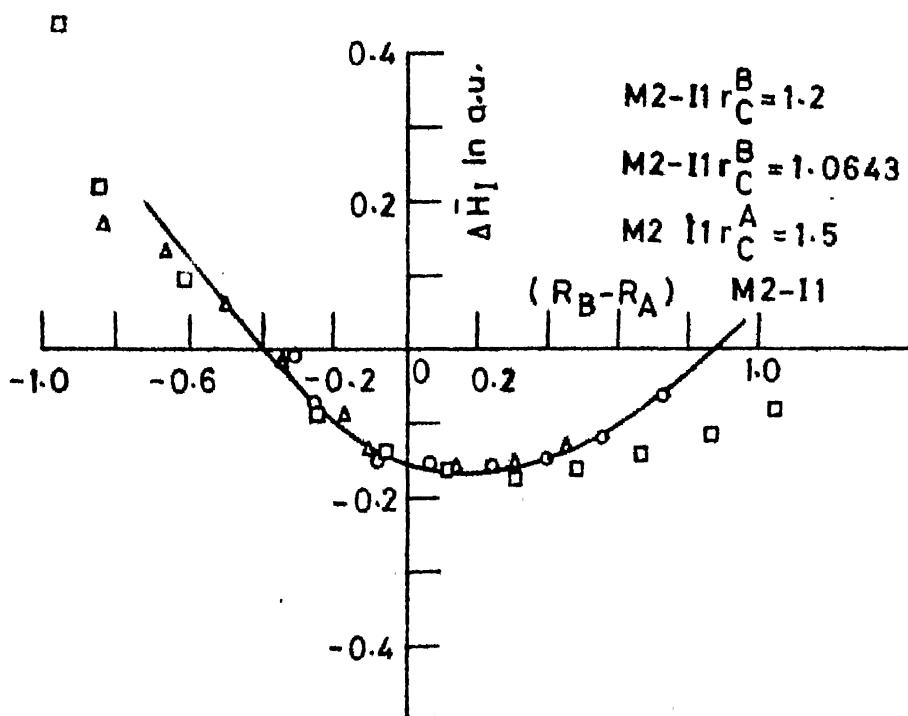
FIG 4.13 : VARIATION OF HEAT OF SOLUTION, $\Delta \bar{H}$, IN CONTINUOUS
MODEL, WITH DIFFERENCE IN ATOMIC RADII OF SOLVENT
AND SOLUTE, $(R_B - R_A)$, IN M2-I1 SYSTEM FOR
DIFFERENT CORE RADII $r_o{}^B = 1.2$ $r_o{}^B = 1.0643$
$r_c{}^A = 1.5$; – EXPERIMENTAL RESULT.

solution are smaller. Thus one can expect that there will be many cases of disagreement between theory and experiment.

Since we have not calculated the heat of solution excepting for the Al-base and Zn-base alloys we devise a method for extrapolating the heat of solution for other systems. Since we see in Fig. 4.11 that the effect of changing r_c of the matrix produces a shift of the $\Delta \bar{\bar{H}}_I$ VS R_A curve keeping their shape almost unaltered, we plot all the data of $\Delta \bar{\bar{H}}_I$ against $R_B - R_A$ in Figs. 4.13 and 4.14. In Fig. 4.13 the squared points are the data for M2 - I1 systems with varying matrix and fixed impurity. The triangular and circled points are from the fixed matrix and varying impurity set for the M2 - I1 systems with r_c^B = 1.0643 and 1.2 respectively. When the size mismatch is small all the points fall on a single line. But they start diverging when the contribution of the size factor to the heat of solution becomes significant. Fig. 4.14 presents similar curves of $\Delta \bar{\bar{H}}_I$ VS ($R_B - R_A$) for the M3 - I2 and M3 - I1 systems.

(c) Comparison with Experiment :

i) Homovalent Case :

Before discussing alloying in the heterovalent case, we collect here experimental results for homovalent simple metallic alloys. Here, within the parameter space

101

Expt. points
□ M3-12
• M3-11

ΔH_I in a.u.

.03

.01

Ga-Ca   Ga-Zn   Ag-Tl   Tl-Zn   M3-11
Hg-In   In-Zn In-Cu
-1.0   -.6   0   .2   Ag-In .6   1.0 $(R_B - R_A)$ in a.u.
-.01
• Au-In
Al-Cu
-.02
• Tl-Na
-.03
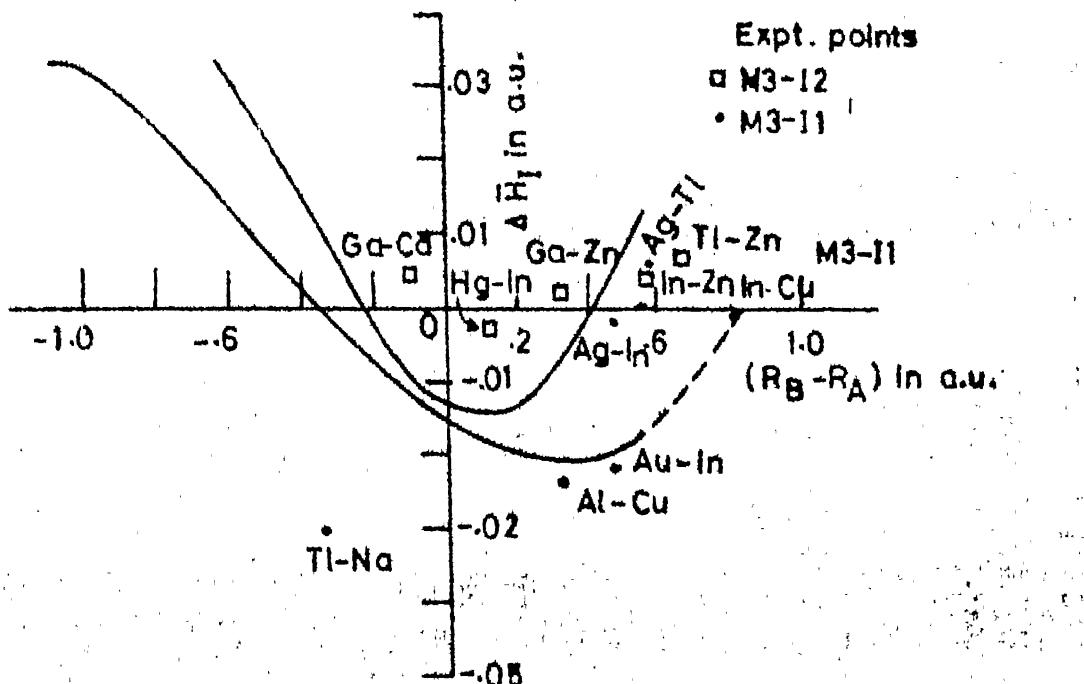
FIG 4.14 : VARIATION OF ΔH_I, IN CONTINUOUS MODEL, WITH (R_B-R_A) FOR (a) M3-12 and (b) M3-11 SYSTEMS.- EXPERIMENTAL RESULTS.

.08   1 M2 11(r_C^A=1.5)
▲ M3-11; r_C^A=1.2
1-Compression
.06
.04   M2 11(r_C^A=1.2)
.02   M2-11 (r_C^A=1.5)
0
.2   .4   .6   .8   1.0   1.2   1.4
$(R_A - R_B)^2$
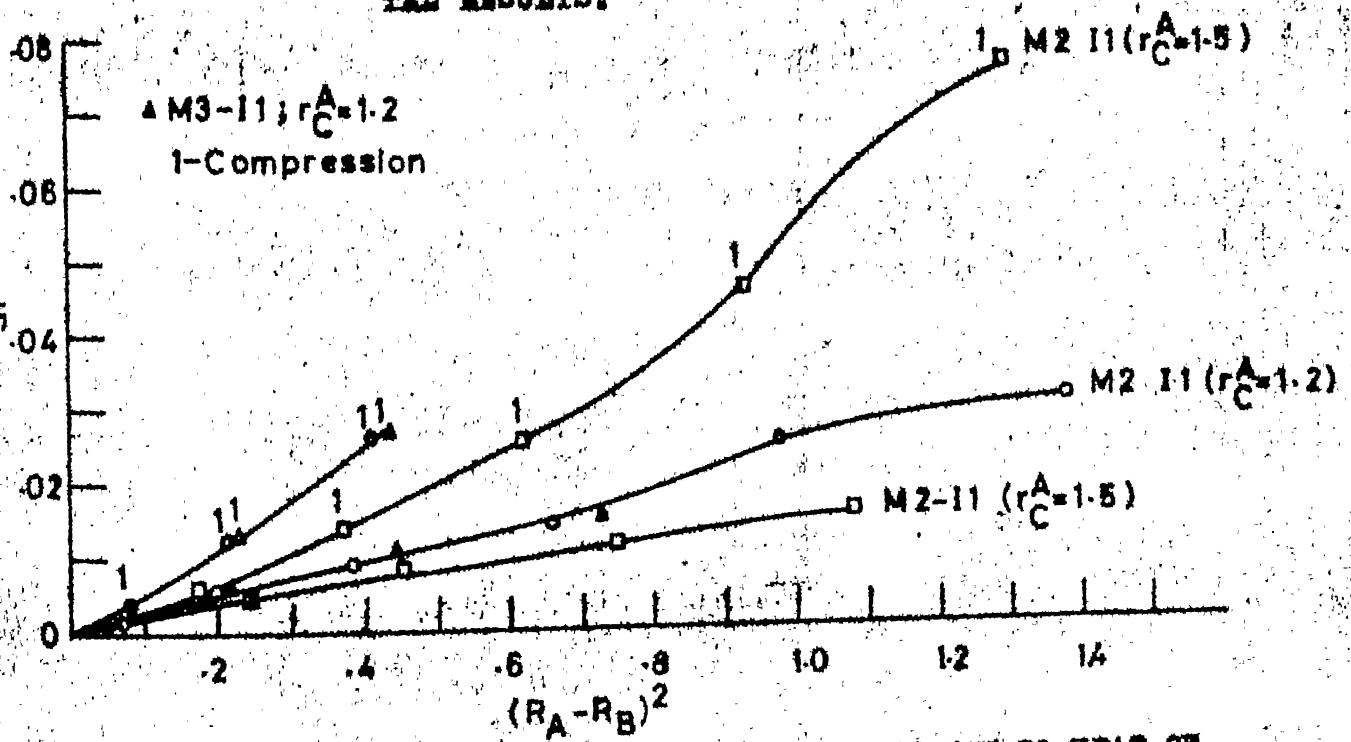
FIG 4.15 : VARIATION OF SIZE FACTOR CONTRIBUTION TO HEAT OF SOLUTION, ΔH_I WITH $(R_B - R_A)^2$ FOR M2-II SYSTEMS WITH (a) $r_0^A = 1.2$ AND (b) $r_0^A = 1.5$ - EXPANSION AND 1-1 COMPRESSION OF SOLUTE. RESULTS FOR M3-II SYSTEM WITH $r_0^A = 1.2$.

chosen by us for the variational method, there is no
step or tanh density profile. The only contribution to the
heat of solution is from the size or atomic volume difference,
this being necessarily a positive term.

In Table 4.2 we show for various valencies, the heats
of solution for AB alloys (both dilute A/and dilute B limits),
and the conditions under which they are measured. The sign
of heat of solution is indicated if that is the only thing
known. We see that while in a number of cases, the heat
of solution is positive, there are nearly as many examples of
negative heats of solution. Thus, the size difference
cannot be the only or dominant factor influencing $\Delta \bar{H}_I$. We
discuss below the various alloys.

In the noble metal alloys, obviously the empty core
description is inadequate. The noble metals have a just
filled d shell, considerable s-d mixing, and the ionic
radius is comparable to the atomic volume radius. Therefore,
there may be electron overlap effects not described in a
simple pseudopotential model.

It is known that in Mg, because there are very
few core orbitals, the core orthogonalization is not very
effective and the 'pseudopotential' is quite strong. In-
deed, many properties of Mg are not well described by a

TABLE 4.2

Partial Molal Heat of Solution of Homovalent Alloys at infinite
EXPERIMENTAL RESULTS   dilution

Type	System A	B	In K cal/gm.atom $\overline{H}_A$	$\overline{H}_B$	TEMP, STATE
M1-I1	Ag -	Au	-4.05	-4.85	800°K, Solid
	Ag -	Cu	9.00	6.00	1052°K, Solid
	Au -	Cu	-4.315	-2.84	720°K, Solid
	Na -	K	+ve small	+ve small	Liquid
M2-I2	Cd -	Mg	-4.13	-2.2	543°K, Solid
	Cd -	Hg	-1.88	-ve	600°K, Liquid
	Cd -	Zn	.2.14	2.25	800°K, Liquid
	Hg -	Zn	+ve	0.71	608°K, Liquid
M3-I3	In -	Tl	.38	.69	623°K, Liquid

pseudopotential. In case of Cd and Hg, both group II B elements, factors similar to those operating for noble metals (large core size, some s-d mixing) are present and thus can lead to negative $\Delta \bar{H}_I$, e.g. for CdHg.

The systems K-Na, Cd-Zn, Hg-Zn, InTl, in which one or both the constituents' are simple metals well described by a simple pseudopotential, all have opositive heats of solution. In the Na-K, Cd-Zn and In-Tl systems the calculated values of $\Delta \bar{H}_{Na} = 1.25$ $\Delta \bar{H}_{Zn} = 5.56$ and $\Delta \bar{H}_{In} = .707$ respectively in the unit of K.cal/gm. atom. These values are of the same order as the experimentally observed ones. The observed trend of increase between these values i.e. $\Delta \bar{H}_{Zn} > \Delta \bar{H}_{In}$ is maintained.

ii) Heterovalent Case ($MZ_B - IZ_A$ with $Z_B > Z_A$)

ii-a) M2 - Il :

As an example of the series of systems studied by us, we discuss here the case where the impurity or solute has a valence 1 and has a given atomic radius R_A (and thus pseudopotential core radius r_c^A). The host has valence 2, and its equilibrium atomic radius is varied by varying r_c^B. This enables us to generate a class of M2 - Il alloy systems with different size and electro-chemical potential differences.

In Table 4.3 we show experimental results for M2 - I1 systems. The sign is shown if it is the only information available. The calculated results are also shown in the table. Actually, the calculations have been carried out for Zn based alloys. The numbers for other cases (Cd and Hg based alloys) have been obtained on bodily shifting the Zn curve by an amount equal to the difference in atomic radii. This procedure gives reliable numbers, provided the compressibilities or size factor effects of the $Z = 2$ hosts do not differ widely and provided these do not dominate the heat of solution. We have shown earlier (Fig. 4.13 , Section 4. 3(a) above) that this is indeed the case for the typical example described there.

We see that except for the case of Hg-K the sign of the heat of solution is correctly given. The right order of magnitude is found for the only two alloys for which $\bar{\bar{H}}_I$ is known experimentally, i.e. Cd-Cu and Hg Na. As will be seen from examples discussed below, we tend to get positive heats of solution for cases of solute compression, i.e. $R_A > R_B$. Experimentally the heats of solution in such cases tend to be more negative than the theoretical value.

ii-b) M3 - I2 and M3 - I1 Systems :

Table 4.4 shows the observed and calculated values of ΔH_I for the above class of systems. Actually, the

TABLE 4.3

$\Delta \bar{H}_I$ for M2 - Il Systems

System M2	Il	Expt. values $\Delta \bar{H}_I$ in a.u. atom of state	Calculated values $\Delta \bar{H}_I$ in au./atom of state	$R_B - R_A$ in a.u.	Temp. State for the expt. results
Cd	Ag	−ve	−.016	+.256	67°K, Solid
	Au	−ve	−.016	+.257	700°K, Solid
	Cu	−.0025	−.01	+.597	875°K, Liquid
	Na	−ve	−.008	+.673	Solid, 298°K
Hg	Ag	−ve	−.014	+.35	Solid, 292°K
	Au	−ve	−.014	+.351	Solid, 550°K
	K	−.0398	+.045	−1.51	Liquid, 600°K
	Li	−ve	−.016	+.094	Solid, 292°K
	Na	−.032	−.016	−.079	Liquid, 298.15°K
Zn	Ag	−ve	−.016	−.104	Solid, 873°K
	Au	−ve	−.016	−.103	Solid, 363°K

TABLE 4.4

$\triangle \bar{H}_I$ for M3 - I1 and M3 - I2 Systems

Type	System		$\triangle \bar{H}_I$(Expt) in a.u/ solute. atom	$\triangle \bar{H}_I$(calcu-lated in an,/ solute atom	$R_B - R_A$	Temp,State for the expt re-sults
	M	I				
M3-I1	Al	Ag	-ve	.032	-1.018	Solid,820°K
		Cu	-.024	-.022	+ .323	Liq,1423°K
	In	Ag	-.0019	-.02	+0.47	Liq,723°K
		Au	-.022	-.02	+.471	Liq,723°K
		Cu	-.0013	-.0015	+.811	Liq,723°K
	Tl	Ag	+.0053	-.016	+.575	Liq,723°K
		Au	-.00008	-.016	+.576	Liq,723°K
		Na	-.03117	-.021	-.354	Liq,648°K
M3-I2	Al	Zn	+.0050	-.014	+.086	Solid,625°K
		Mg	-.021	+.01	-.355	Liq,723°K
	Ga	Cd	+.0049	-.008	-.104	Liq,700°K
		Zn	+.0019	-.011	+.256	Liq,723°K
	In	Hg	-.0028	-.014	+.120	Liq,433°K
		Cd	-.0018	-.013	+.214	Liq,723°K
		Zn	+.0042	+.013	+.574	Liq,700°K
	Tl	Hg	-ve	-.012	+.225	Liq,293°K
		Cd	+.0028	-.007	+.319	Liq,673°K
		Zn	+.0067	-	+.679	Liq,1099°K

calculations were done for Al based alloys and the numbers for In, Ga and Tl based alloys have been obtained by shifting the $\Delta \bar{\bar{H}}_I$ curves as described earlier above (This section 4.2(ii)). Again, the sign of $\Delta \bar{\bar{H}}_I$ is generally given correctly. The heat of solution is often overestimated in many good pseudopotential cases where there are no problems due to large core, s-d mixing, etc. the agreement is fairly good. In many cases, we obtain the correct trend, e.g. in In-based alloys, as the solute changes (Hg, Cd, Zn), the size difference increases, and so does the heat of solution. Our obtaining too large negative values may be partly due to inaccurate estimate of the size factor effect. The trend in Tl(Cd, Zn) is also correctly reproduced.

(d) Factors Affecting the Alloys :

In the first chapter we have already discussed the state of present understanding of the factors affecting the alloying process namely, the size factor effect and the electro-chemical effect. In Chapter 3 we have presented an account of the variational models - the step model and the continuous model. It has also been pointed out there how in the step model these two factors can be separately estimated and assessed inspite of the crudity of this model. In the continuous model this advantage

is lost. In the following sub-sections we are going to discuss these two factors in view of our calculated results.

(i) Size Factor Effect : It is, as explained in Chapter 3 through figure 3.1(c), the energy spent to prepare a solute atom so that it fits snugly in the solvent lattice site. With the help of eqn. (3.14) we can write this energy $\Delta E_{S.F}$ as

$$\Delta E_{SF} = \left. E_A^{alloy} \right|_{r_{st} = R_B} - E_A^{pure} \tag{1}$$

In our computation we take a monovalent solute of core radius $r_c^A = 1.2$ and put it in a matrix of valence 2 or 3 (M2 or M3). The matrix is immaterial here since what we study essentially is the expansion and compression behaviour of an atomic cell of the solute of valency 1 and core radius 1.2. The results are presented in the form of plot of ΔE_{SF} vs $(R_A - R_B)^2$ in Fig. 4.15. The points marked by 1 represent the path of energy during compression. We also repeat the calculation with solute core radius $r_c^A = 1.5$ to study its effect and these results are identified by squared points in the same figure.

The general features of these curves are as follows :
(1) There is a linear region when the deformation is small (2) This linear region extends upto larger

$(R_A - R_B)^2$ for expansion as compared to ⸴⸴ compression.
(3) The compression involves higher energy than expansion
for the same amount of deformation. (4) As the core radius
increases the strength of the material reduces and hence
the $r_c^A = 1.5$ curve lies lower compared to that of $r_c^A = 1.2$.

These characteristics described above are quite
expected and can be understood easily. The point we should
note is the severe limitation of the elastic continuum
theory to describe solid solution when $R_B < R_A$. For
$R_A < R_B$ this theory should work well to quite a large
extent of size-mismatch. The general belief of symmetric
behaviour with respect to $(R_A - R_B)^2$ is not confirmed.
This explains the asymmetry in the M3 - I3 curve of Fig.
4.10. This asymmetry is much more pronounced in $\Delta \overline{\overline{H}}_I$
curves of Fig. 4.10 for non-homovalent system because of
the additional **effect of the** electro-chemical factor.

(ii) The Electro-chemical Factor : The electro-chemical
contribution to the heat of solution is the energy change
connected with the charge transfer between the solute cell
and the surrounting solvent matrix. In the step model when
$r_{st} = R_B$ i.e. the configuration where the solute atom has
undergone a dilation or compression to fit the solvent site,
there is no charge transfer and the energy to be expended

to attain this configuration is termed the size factor con-
tribution as explained in the previous sub-section. It
corresponds to Fig. 3.1(c). Now this charge density is not
the ground state charge density in the alloy and so a further
re-distribution of charge takes place leading to a charge
transfer. This results in a surface dipole at the interface
between the solute and the solvent. This reduces the energy
of the system. The charge transfer i.e. the dipole forma-
tion, will be opposed by an increase in the kinetic and the
electron-electron interaction energy of the system. A balance
between these two opposing trends will lead to a minimum
corresponding to the ground state energy of the alloy (Fig.
3.1(d)). In view of the above discussion we can write the
energy contribution $\Delta E_{e.c}$ due to electro-chemical changes
as

$$\Delta E_{e.c} = \Delta \bar{H}_I - \Delta E_{S.F.} \tag{2}$$

Now Pauling's[2] rule states that the electro-chemical contri-
bution to the heat of solution is proportional to the square
of the difference in the electro-negativities of the consti-
tuents. On the basis of similarity of this expression with
that obtained from density functional theory. Hodges and
Stott[3] have attributed a precise meaning to the concept of
electro-negativity by identifying it with the chemical
potential (See Chapter 1). Our attempt will be to analyse
these data ($E_{e.c}$) on the basis of chemical potential.

The chemical potential μ can be defined for solid in the following way. From eqn. (3.1) the ground state energy of a system $E[n]$ can be written as a functional of its correct ground state density in the standard way.

$$E[n] = G[n] + \int v_{ext}(\vec{r})\, n(\vec{r})\, d\vec{r} + \frac{1}{2} \int \frac{n(\vec{r})\, n(\vec{r'})}{|\vec{r} - \vec{r'}|}\, d\vec{r}\, d\vec{r'} \qquad (3)$$

where $G[n] = T[n] + E_{xc}[n]$

If we define,

$$\phi(r) = v_{ext}(\vec{r}) + \int \frac{n(\vec{r'})}{\vec{r} - \vec{r'}}\, d\vec{r'} \qquad (4)$$

$$\text{then,} \quad \mu = \frac{\partial E[n]}{\partial n} = \frac{\partial G}{\partial n(r)} + \phi(r) \qquad (5)$$

If ϕ and the functional derivative of G are known even at one point inside the system then μ can be found out by eqn. (5). Seitz[42] has given an expression for the uniform electron gas of density n placed in the field of a charge − Z as follows.

$$\mu = -U + \mu_u(n) - \varepsilon(n) + \frac{3}{5}\frac{Z}{R} \qquad (6)$$

where, −U is the binding energy of the solid, $\mu_u(n)$ is the chemical potential of a uniform gas, $\varepsilon(n)$ is the energy of a electron gas of density n and the last term gives the Coulomb self energy. Eqn. (6) assumes a uniform electron gas in a Wigner Seitz Cell. Such an assumption is incompatible with eqn. (5) since if $\phi(r)$ varies with r, then

$\frac{\partial G}{\partial n}$ must vary in a compensating manner to give a constant μ throughout the system at thermodynamic equilibrium. It clearly shows that eqn. (6) is obtained by averaging over a WS cell.

Looking at eqn. (5) we notice that near the edge of a WS cell $\phi(r) = 0$ and if the density here is $\bar{n}$ the chemical potential is given by

$$\mu_u = \frac{\partial G}{\partial n}\Big|_{n = \bar{n}} \tag{7}$$

This is just the chemical potential of a uniform electron gas of density $\bar{n}_o$. This would be the the correct μ to use in discussing charge transfer etc., if the charge transfers were confined to a small region near the surface of the WS cell. However, our calculations show that this is not the case. Therefore, it makes better sense to define the electro-chemical potential using (5) and averaging over the unit cell. For the case of an empty core pseudopotential, this gives

$$\mu = \mu_u(n) + \frac{Ze^2}{R}\left[\frac{3}{2}\left(\frac{r_c}{R}\right)^2 - \frac{3}{10}\right] \tag{8}$$

where R is the atomic radius, and r_c the core radius of the pseudopotential. The electro-chemical potential now depends not only on density n but also on the ionic or core radius r_c. We plot in Fig. 4.16 $\mu_u(n)$, as a function of r_s, and also μ calculated according to Eq. (8) for the

113

FIG. 4.16: VARIATION WITH r_s OF (a) CHEMICAL POTENTIAL OF UNIFORM FREE ELECTRON GAS, μ_u, AND (b) CHEMICAL POTENTIAL OF A SYSTEM WITH IONIC PSEUDO-POTENTIAL ($Z=2.0$).

case $Z = 2$. In the latter case, r_c is varied to give
different equilibrium values of R and thus r_s $(= R/Z^{1/3})$.
We notice that while the general trend of variation with
r_s is the same in both cases, in the latter case the ionic
attraction makes a large negative contribution for small r_c
(and therefore, small R and r_s). As R increases this con-
tribution decreases (See Eq. (8)) and the chemical potential
approaches that of the free electron gas. The large di-
fference between the two shows that the role of the ionic
potential is quite significant.

In Figs. (4.17) and (4.18), we show $\triangle Q$, $(\mu_B - \mu_A)$ and $\triangle \bar{H}_I$
for the case of a fixed impurity (with $Z_A = 1$) in a matrix
$(Z = 2)$ of varying size. In Fig. 4.17, we show the charge
transfer to the solute cell (in units of e) as a function of
$\mu_B - \mu_A$. The charge transfer is for the tanh case, and has
been calculated by integrating the density $n(r)$ upto $r = R_B$
(i.e. over W.S. cell where the solute is located), and
subtracting the solute charge Z_A. μ_B is the electro-
chemical potential calculated according to Eq. (8). Clearly,
the physically appropriate μ_A corresponds to that confi-
guration of μ_A which has the atomic radius R_B. We notice
that the relation $\triangle Q = \lambda(\mu_B - \mu_A)$ is not satisfied. How-
ever, the charge transfer does increase with increasing
$(\mu_B - \mu_A)$, and there is a large linear region. We also
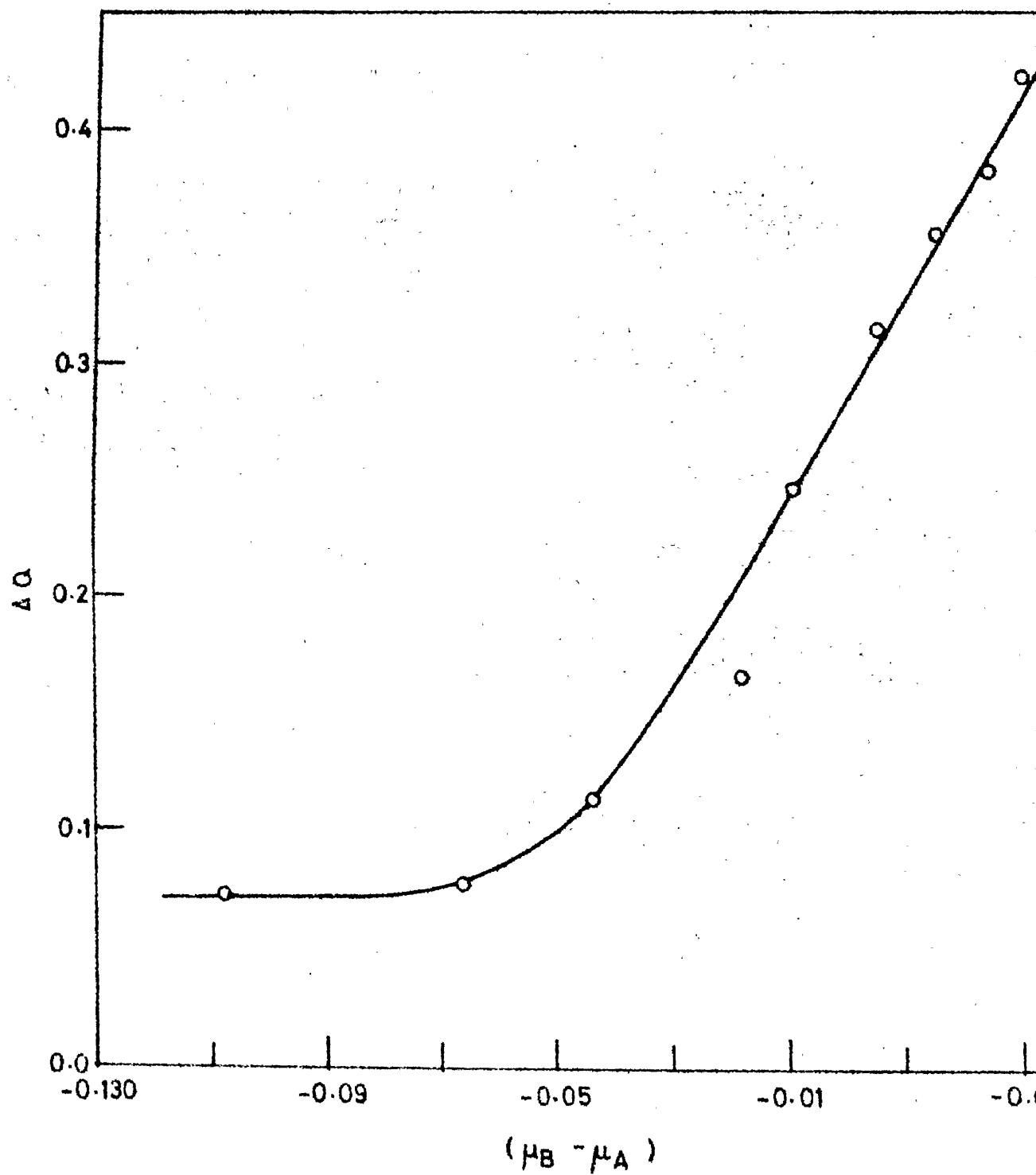
FIG 4.17 : VARIATION OF CHARGE TRANSFER TO SOLUTE WS CELL, ΔQ
WITH DIFFERENCE IN CHEMICAL POTENTIAL BETWEEN
SOLVENT (B) AND SOLUTE (A), $(\mu_B - \mu_A)$.

find that rather large charge transfer ($\Delta Q \sim 0.4$) takes place in these model systems. The reason for charge transfer to solute is the following. The kinetic energy term favours transfer of electrons from a high to low density region. Transfer to solute reduces the density inhomgcnity, and is favoured by the gradient term. The electron electron repulsion is comparatively less if charge flows away from high charge density to a low charge density region. The ionic potential ofthe solvent acts in the opposite direction. It is not clear to us, from this model system study, that the charge transfer can be quantitatively obtained from the electro-chemical potential difference from a simple formula such as $\Delta Q \propto (\mu_B - \mu_A)$.

Figure 4.18 shows $\log_{10} \Delta E_{e.c.}$ plotted as a function of $\log_{10} \Delta Q$. We remark that both of these are theoretically calculated quantities, and the electro-chemical potential does not intervene. We find that $\Delta H_{e.c.} \propto \Delta Q^{1.4}$. $E_{e.c.}$ does go up with ΔQ, but not quadratically as predicted by simple theories and conjectures.

In Fig. 4.19 we plot another interesting systematic feature, namely ΔQ for the case where the matrix is fixed, and impurity or solute size is varied by varying its pseudopotential core radius. In this case, if we imagine
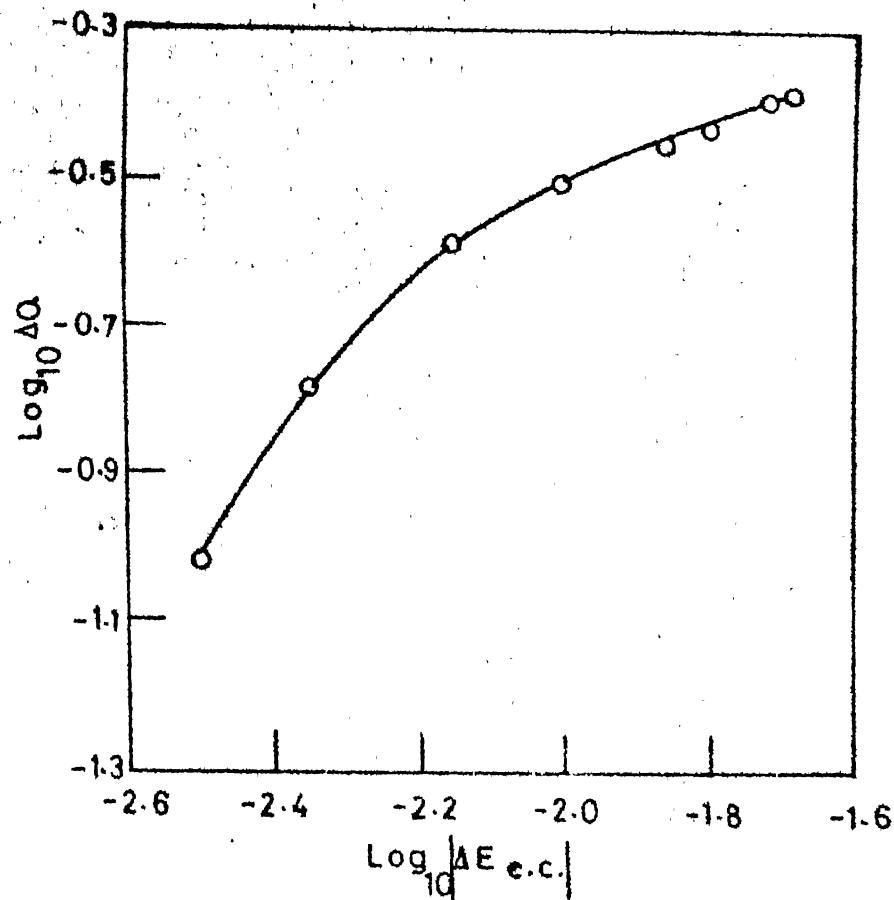
FIG 4.18 : LOGARITHMIC VARIATION OF ELECTRO-CHEMICAL
CONTRIBUTION TO THE HEAT OF SOLUTION, $\Delta E_{e.c.}$
WITH CHARGE TRANSFER FOR M2 – Ti SYSTEM WITH
$r_0 A = 1.5$ IN CONTINUOUS MODEL.
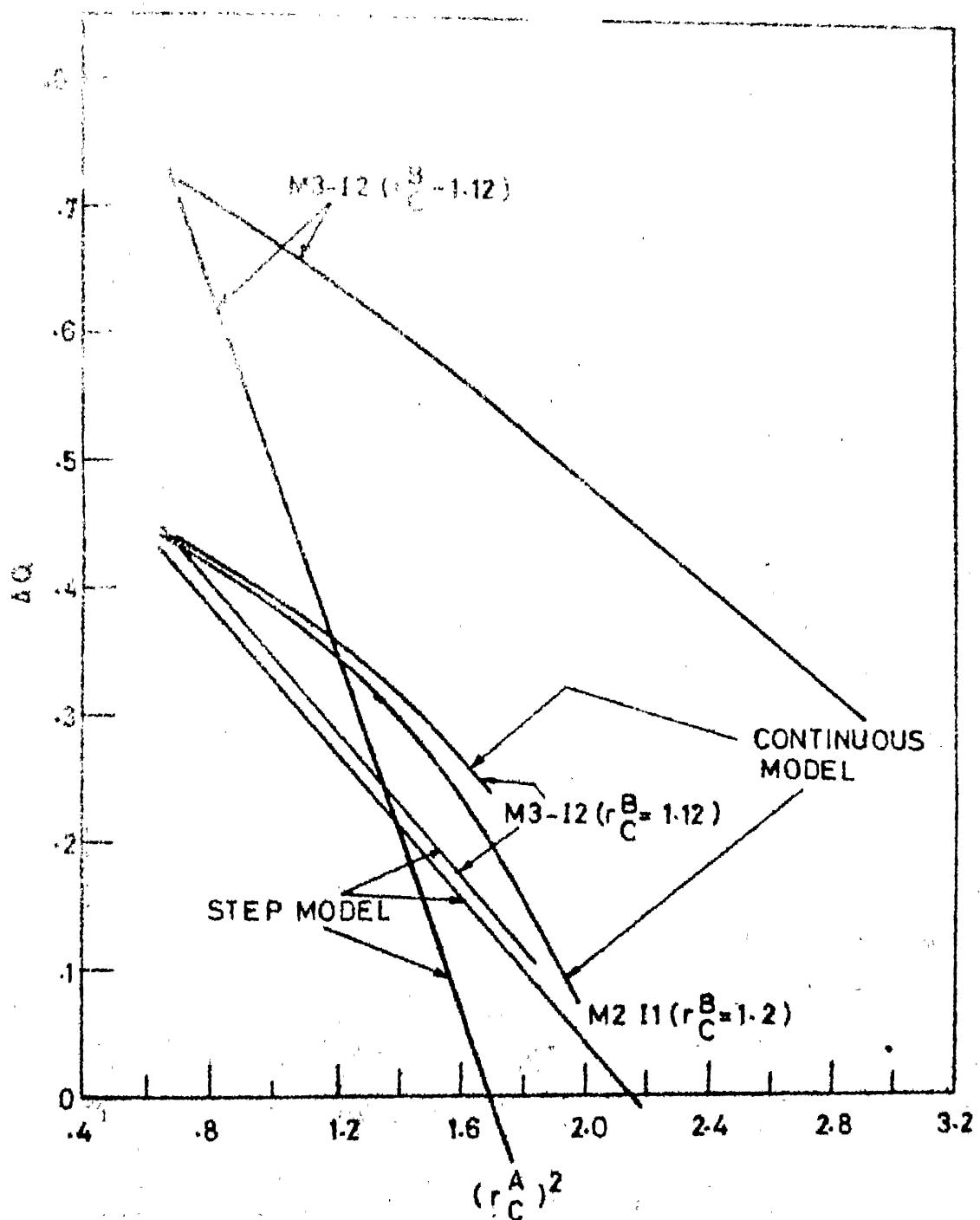
FIG 4.19 : VARIATION OF CHARGE TRANSFER, △ Q WITH SQUARED
CORE RADIUS OF SOLUTE, (r_c^A)² FOR (a) M3 – I2
(b) M3 – I1 and (c) M2 – I1 SYSTEMS;
◦: CONTINUOUS MODEL AND � : STEP MODEL.

the solute to be compressed or expanded to solvent atomic

radius, the chemical potential difference would be constant

if it were to depend only on electron density. In that

case, $\triangle Q$ should be constant. The fact that $\triangle Q$ varies widely

indicates that the ion potential contribution to μ is

important. Since the only thing that varies is r_c^A, and

$\mu_A \propto r_c^{A^2}$ (see Eq. (8)) we expect that $\triangle Q \propto (\mu_B - \mu_A)$

$\propto (-r_c^{A^2})$ and would decrease as r_c^A increases. This is indeed

what we find. In Fig. (4.18) we have plotted $\triangle Q$ vs $r_c^{A^2}$

for several systems, i.e. M3 - I2, M3 - I1 and M2 - I1. Both

the step model (marked s) and continuous model (marked c)

results are shown. The charge transfer is more in the tanh

or continuous model because of the possibility of charge

relaxation in attaining a continuous distribution.

4.4 The Problems Encountered in Alloys with Higher Valence
    Solute :

Figure 4.7(a) and (b) shows the results of fixed matrix

and varying solute r_c^A results for M1 - I2, M1 - I3 and M2 - I3

systems where although $r_{st} < R_B$ in the step model and

$r_c < R_B$ in the continuous model the $\triangle \bar{\bar{H}}_I$ is negative. This

is not acceptable because the variationally arrived at

electron distribution shows that the matrix is intact and

the solute cell charge density has undergone a redistribution

there being no charge transfer. Now if we

had started with the correct ground state charge density of the solute then any re-distribution of energy of charge within the solute cell would lead to an increase in energy i.e. E_A^{alloy} would be greater than E_A and hence $\triangle \bar{H}_I$ must be positive.

To correct this situation we attempted to start with a better ground state charge distribution of the solute given by the cosine model. The alloy charge density was taken as

$$n(\vec{r}) = n_B^o - B_1(1 + \cos \pi r/R_A)\,\theta\,(R_A - \vec{r}) +$$
$$B\,(1 - \tanh\,\beta(\vec{r} - r_o)) \qquad (9)$$

where B_1 is the amplitude of the cosine term of pure solvent charge density in our cosine model. This $n(\vec{r})$ given by eqn. (9) has three floating parameters B, r_o and β one of which can be determined from charge neutrality and the other two are determined variationally. This calculation was conducted for M1 - I2 set and the results show that the continuous model M1 - I2 curve of Fig. 4.9(a) is pushed up (see Fig. 4.20 where the two are compared) but still we get a negative region upto $r_c^A = 1.1$ with the maximum depth at $r_c^A = 0.8$. This probably might mean that if the ground state charge density is calculated in a more accurate model the physical inconsistency of the results
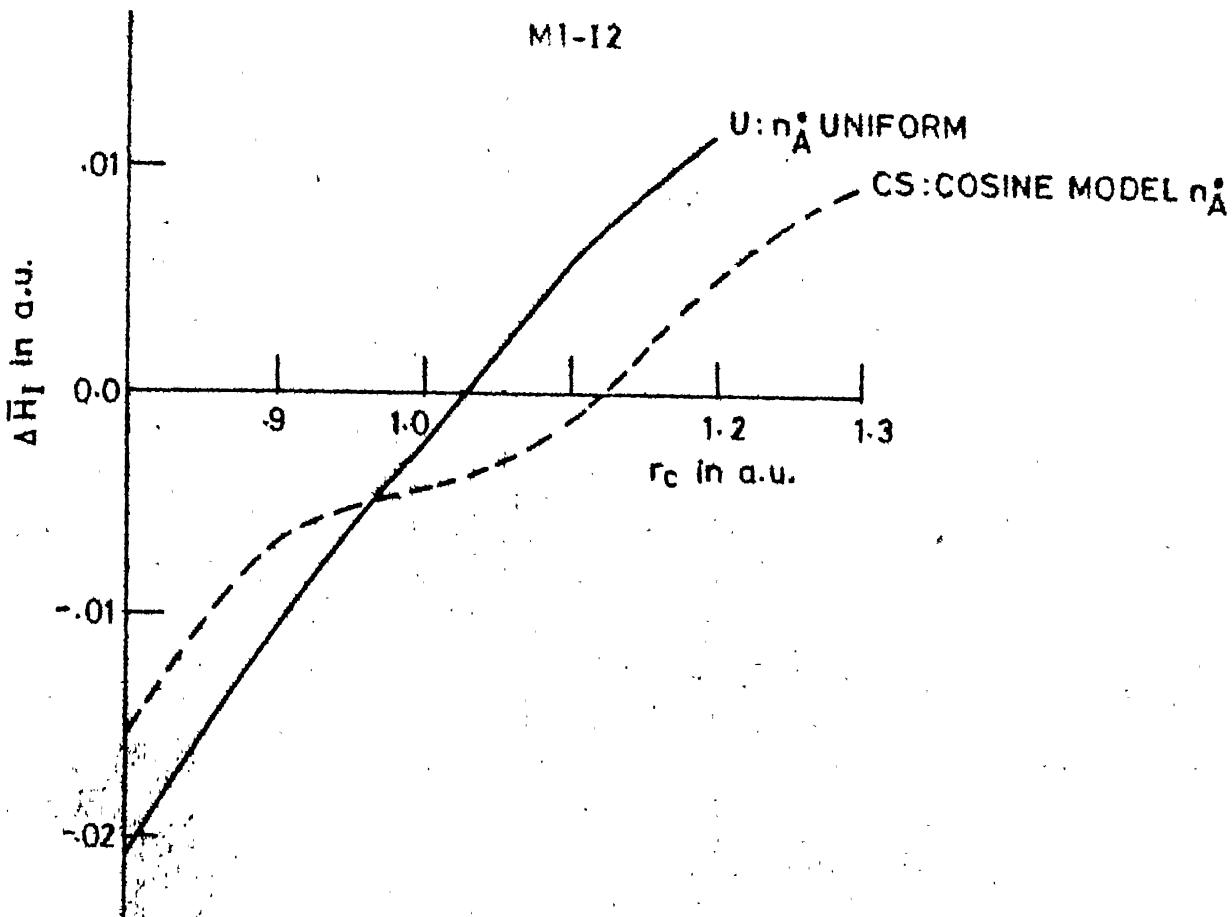
FIG 4.20 : EFFECT OF GROUND STATE CHARGE DENSITY (GSD) OF SOLUTE ON HEAT OF SOLUTION, $\Delta \bar{H}_I$ V_S SOLUTE CORE RADIUS, r_c A CURVE IN M1 - I2 SYSTEM, U-UNIFORM SOLUTE GSD AND CS-COSINE MODEL SOLUTE GSD.

may be eliminated.

The variational parametrization is perhaps quite unsuitable for $Z_A > Z_B$ because in these cases there is probably a long range charge transfer extending in the matrix much beyond the next nearest neighbour. Our numerical schemes search for a minimum in general upto r_{st} or r_o equal to 2 R_B. In some cases we find a minimum with r_{st} located well inside the core region of the solvent. Unfortunately, because we are working with a pseudopotential such results are not reliable.

Chapter 5

Kohn-Sham Method in Metals and Alloys

In this chapter we describe how the Kohn-Sham method (presented in Chapter 2) can be reformulated in the case of metals and alloys as a system of weakly interacting pseudo-atoms. In contrast to the parametric variational scheme, here no assumption is made about the form of $n(\vec{r})$ which is calculated directly by solving a Schrodinger like equation obtained variationally by Kohn and Sham[19] from the density functional for the ground state energy. The $n(\vec{r})$, thus determined, defines the system uniquely and helps to find out the different ground state properties.

In Section 1 we visit the concept of pseudoatom again as an extension to the discussion contained in Chapter 2. Then we present in Section 2, method for calculating the ground state energy and hence the cohesive energy of pure metals. In Section 3 we describe the scheme for calculating the heat of solution of alloys. The last section contains the preliminary results obtained for the cohesive energy of Al, Mg and the heat of solution of the Al-Mg alloy.

5.1 Pseudo-atom in Metals :

This idea as already explained in Chapter 2, is that a metal may be treated in some respects as if it were an

assembly of neutral 'atoms'. These atoms are not the same
as the objects we get if we take the metal to pieces
and put the right number of valence electrons around each
ion. In the metal, an ion is positively charged, but it
is immersed in the gas of conduction electrons, which tend
to distribute themselves so as to form a screening cloud
about each ion. The basic contention is that the object
composed of the ion and the screening charge can be treated
as the unit for building the structure. This is how
Ziman[43] puts forward this concept in his pioneering article
although this idea was shared for quite some time by many
other research workers like, Heine, Harrison, Phillips[4.3].
From the view-point of the density matrix, the idea has been
developed by March and co-workers[44].

The above concept does not mean that the conduction
electrons are localized. They form the usual highly degene-
rate Fermi gas. But the scattering of electrons from an
array of pseudo-atom ordered or disordered can be treated
without any need to consider further shift of charge to
maintain local neutrality. Moreover, inspite of the strong
potential inside the core the scattering from each 'pseudo-
atom' is quite weak and so may be treated as a pertur-
bation due to a small 'effective potential' carried by the
atom. If this effective potential is known one can set out

to calculate the band structure, the shape of the Fermi-surface, resistivity etc. properties as shown by Ziman[43].

Despite its simplicity this kind of model yields a self consistent scheme of calculation as will be shown in the next section. It has also been shown by the calculation of Dagens[9] that the effective inter-atomic potential or pseudo-atom-pseudo-atom interaction is small as expected. But one of the defects of this model is that it assumes free electron states for the valence states. A nearly free electron formulation of this aspect is possible but poses a good deal of difficulties in achieving self-consistency. The linearised superposition that is used in constructing the system has got some errors associated with it but it will be much smaller than that will arise when one tries to do screening after disturbing the lattice.

With the above preface to the treatment of metals by this model we proceed to present the formulation for cohesive energy of metals in the following sections.

5.2 Cohesive Energy of Pure Metal :

Here we find the cohesive energy of pure metals using a neutral pseudo-atom model. The basic idea is to express the total energy as the sum of individual pseudo-atom energies and their pairwise interactions. To make this

approach practicable one has to formulate it in a precise, rapidly convergent scheme. Below we present our version of this formulation which has been used in our study.

From eqn. (14) of Chapter 2 we can write the total energy, $E[n]$ of a system of electron gas with density $n(\vec{r})$ as

$$E[n] = T[n] + E_{xc}[n] + \int v_{ext}(\vec{r})\, n(\vec{r})\, d\vec{r} +$$

$$\frac{1}{2} \int \frac{n(\vec{r})\, n(\vec{r}')}{|\vec{r} - \vec{r}'|}\, d\vec{r}\, d\vec{r}' + V_{ii} \qquad (1)$$

where V_{ii} is the electrostatic interaction between the ions and the other terms as defined before. So, if one knows $n(r)$ correctly and the functional forms of $T[n]$ and $E_{xc}[n]$, the ground state energy $E[n]$ is completely defined. If one conceives the electron density in each neutral pseudo-atom to consist of a uniform part n_0 and a deviation δn, from it on account of non-uniform charge polarisation due to screening one can write the electron density of the system as

$$n(\vec{r}) = n_0 + \sum_i \delta n\, (\vec{r} - \vec{R}_i) \qquad (2)$$

This is same as eqn. (28) of Chapter 2. Here the periodic density in metals has been split into a uniform part and an oscillatory part $\delta n(\vec{r} - \vec{R}_i)$ centred around each Wigner-Seitz cell at lattice vector positions $\vec{R}_i$'S. Since each

pseudo-atom is neutral it follows that

$$\int \delta n \, (\vec{r} - \vec{R_i}) \, d\vec{r} = 0 \qquad (3)$$

Now the problem reduces to finding out δn in one neutral pseudo-atom in the metal and thereby to find out the cohesive energy from eqn. (1). In both of these stages approximations are made. In calculating $\delta n(r - R_i)$ it is assumed that only the ionic potential due to centre i is non-zero and the total energy is assumed to consist of only one centre and two centre terms. The significance of these assumptions will be dealt with to give a clear understanding of this method.

Following eqn. (24) of Chapter 2 one can write the effective potential as

$$V_{eff}[n(\vec{r})] = V_{ext}(\vec{r}) + \mu_{xc}[n] + \int \frac{(n(\vec{r}'))}{|\vec{r} - \vec{r}'|} \qquad (4)$$

The approximation involved at this phase is in writing

$$V[n(\vec{r})] = V[n_0 + \sum_i \delta n(\vec{r} - \vec{R_i})]$$

$$\simeq \sum_i V(n_0 + \delta n(\vec{r} - \vec{R_i})] \qquad (5)$$

The correction term is given by

$$V[n(\vec{r})] - \sum_i V[n_0 + \delta n(\vec{r} - \vec{R_i})] = \sum_{i,j} \delta n_i \, \delta n_j \left(\frac{\partial^2 V}{\partial n_i \partial n_j}\right) \qquad (6)$$

The omission of this second-order term in potential will affect the wave function ψ in fourth order, i.e. $O(\delta n_i \, \delta n_j)^2$ or $O(\delta n)^4$. This can safely be neglected if δn is small, or if the overlap between δn_i and δn_j is small.

The neglect of all other centres excepting the centre i can be understood easily in terms of Green's function. If we define

$$G(\vec{r},\vec{r}',w) = \int < \{\psi^+(\vec{r},t) \; \psi(\vec{r}',0)\} > e^{-iwt} \, dt \qquad (7)$$

Then the density of electrons is given by

$$n(\vec{r}) = \frac{1}{\pi} \int_{\infty}^{\infty} I_m \; G(\vec{r},\vec{r}',w) \; dw \qquad (8)$$

If we write $G(\vec{r},\vec{r}',w) = G^O(\vec{r},\vec{r}',w)$ when $V_{ext} = 0$, we can calculate G in terms G^O as shown by the diagrams below.

$$G = \quad \overset{i}{\underline{\qquad}} \quad + \quad \overset{i}{\triangle} \quad + \quad \overset{i}{\triangle} \quad + \; \ldots\ldots\ldots \qquad (9a)$$

$$+ \quad \overset{i \quad j}{\underline{\qquad}} \quad + \; \ldots\ldots \qquad (9b)$$

The effect of assuming all other potentials absent is equivalent to neglecting all the terms of class (9b) or multi-centre scattering terms. But the scattering from centre i is taken care of to all orders. This approximation will lead to an error of $O(V_{ij}^2)$ in δn and hence an error of $O(V_{ij}^4)$ in energy. So, we can conclude that it is reasonable to calculate $\delta n(\vec{r} - \vec{R}_i)$ in this one centre

approximation.

Following eqn. (4) one can write

$$V_{eff}[n(\vec{r})] = \sum_i V_{ext}^i(\vec{r}) + V_{xc}[n(\vec{r})] + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

$$= \sum_i V_{ext}^i(\vec{r}) + \{V_{xc}[n_0 + \sum_i \delta n(\vec{r}-\vec{R}_i)] - V_{xc}[n_0]\} + V_{xc}[n_0] + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

$$= \sum_i V_{ext}^i(\vec{r}) + \sum_i [V_{xc}(n_0+\delta n(\vec{r}-\vec{R}_i)] - V_{xc}[n_0]] + \sum_i \int \frac{n_0^i+\delta n(\vec{r}-\vec{R}_i)}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{xc}[n_0]$$

$$= \sum_i [V_{ext}(\vec{r}) + \delta V_{xc}^i + \int \frac{n_i(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}'] + V_{xc}[n_0] \tag{10}$$

where n_0^i is the uniform density in the ith Wigner-Seitz cell and $n_i(\vec{r}')$ is the density of electrons in that cell.

The term $V_{xc}[n_0]$ in eqn. (10) can be taken care of while calculating $E[n(\vec{r})]$. It corresponds to a constant energy shift and so does not affect the calculation of $\delta n(\vec{r}-\vec{R}_i)$ which is to be used in solving the Schrodinger-like equation expressed by eqn. (25) of Chapter 2.

$$h \psi_\lambda^i(\vec{r}) = \varepsilon \; \psi_\lambda^i(\vec{r}) \tag{11}$$

where

$$h = - \nabla^2 + V_{ext}^i(\vec{r}) + \{V_{xc}[n_0 + \delta n(\vec{r}-\vec{R}_i) - V_{xc}[n_0]\} +$$

$$\int \frac{[n_0^i + \delta n(r-R_i)]}{|\vec{r} - \vec{r}'|} d\vec{r}' \tag{12}$$

Now $\delta n(\vec{r} - \vec{R}_i)$ is given by

$$\delta n(\vec{r} - \vec{R}_i) = \sum_{\lambda_{occ}} |\psi_\lambda^i(r)|^2 - n_0 \qquad (13)$$

This three equations from (11) to (13) can be solved self-consistently to get $\delta n(\vec{r} - \vec{R}_i)$.

For $V_{ext}^i(\vec{r})$ one should have the ionic potential, i.e., suppose for the appropriate ionic configuration, the wavefunction hence the charge density $\rho_{ion}(r)$ is known. Then, the coulomb potential is given by

$$V_{coul}^i = \int \frac{\rho_{ion}(\vec{r'})}{|\vec{r} - \vec{r'}|} d\vec{r'} \qquad (14)$$

In addition, the conduction electrons and the ion-core electrons being both identical fermions will exchange and correlate. This contribution is given by

$$V_{xc}^i(\vec{r}) = V_{xc}[\rho_{ion}(\vec{r}) + n_0 + \delta n(\vec{r} - \vec{R}_i)] - V_{xc}[\rho_{ion}(\vec{r})]$$

$$- V_{xc}[n_0 + \delta n(\vec{r} - \vec{R}_i)] \qquad (15)$$

Now the V_{ext}^i is given by

$$V_{ext}^i = V_{coul}^i + V_{xc}^i \qquad (16)$$

But in our study we do not calculate the V_{ext}^i by this procedure. Instead we use a pseudopotential whose choice will be described in the next section. This pseudo-potential simulates the effect of V_{ext}^i given by eqn. (16) in a given

and $E[n_o] = \sum_{i,k < kF} \varepsilon_{kF}^{oi} + \int \{ \varepsilon_{xc}[n_o] - \mu_{xc}[n_o] \} n_o \, d\vec{r}$

$$- \tfrac{1}{2} \int \frac{n_o n_o \, d\vec{r} \, d\vec{r}'}{|\vec{r} - \vec{r}'|} + V_{ii} \qquad (19)$$

Subtracting eqn. (19) from (18) we will be left with the ΔU_I's and ΔU_{II}'s. First let us evaluate the change in one centre terms ΔU_I's. From phase shift analysis we can write

$$\sum_{k < kF} (\varepsilon_k^i - \varepsilon_k^{oi}) = \frac{2}{\pi} \sum_{\ell} \int_0^{\varepsilon_F} \frac{d\delta(\varepsilon)}{d\varepsilon} \varepsilon \, d\varepsilon$$

$$= -\frac{2}{\pi} \sum_{\ell} \int_0^{\varepsilon_F} (2\ell+1) \, \delta(\varepsilon) d\varepsilon - \frac{2}{\pi} \sum_{\ell} (2\ell+1)[\delta_\ell(\varepsilon_F) - \delta_\ell(0)]\varepsilon_F$$

$$= -\frac{2}{\pi} \sum_{\ell} \int_0^{\varepsilon_F} (2\ell+1)\delta_1(\varepsilon) d\varepsilon - \frac{2\Delta Z}{\pi} \varepsilon_F \qquad (20)$$

In the case of pure metals $\Delta Z = 0$, so only the first term in eqn. (20) survives.

Now we set out to find the change in the exchange and correlation terms given by

$$\int \{ \varepsilon_{xc}[n(\vec{r})] - \mu_{xc}[n(\vec{r})] \} n(\vec{r}) d\vec{r} - \int \{ \varepsilon_{xc}[n_o] - \mu_{xc}[n_o] \} n_o dr$$

Sorting out the one centre terms from this expression we get a contribution of

$$\sum_i \int (\delta\varepsilon_{xc}^i - \delta\mu_{xc}^i) [n_o + \delta n(\vec{r} - \vec{R}_i)] d\vec{r} \qquad (21)$$

where $\delta\varepsilon_{xc}^i = \varepsilon_{xc}[n_o + \delta n(\vec{r} - \vec{R}_i)] - \varepsilon_{xc}[n_o]$

and $\delta\mu_{xc}^i = \mu_{xc}[n_o + \delta n(\vec{r} - \vec{R}_i)] - \mu_{xc}[n_o]$

The change in coulomb term can be written as

$$-\tfrac{1}{2} \int \frac{n(\vec{r}) \; n(\vec{r})}{|\vec{r} - \vec{r}'|} \; d\vec{r} \; d\vec{r}' + \tfrac{1}{2} \int \frac{n_o \; n_o}{|\vec{r} - \vec{r}'|} \; d\vec{r} \; d\vec{r}'$$

and after sorting out the one centre terms we get

$$- \sum_i n_o \int \frac{\delta n (\vec{r}' - \vec{R}_i)}{|\vec{r} - \vec{r}'|} \; d\vec{r} \; d\vec{r}' - \sum_i \int \frac{\delta n_i(\vec{r}) \; \delta n_i(\vec{r}')}{|\vec{r} - \vec{r}'|} \; d\vec{r} \; d\vec{r}' \quad (22)$$

We write these terms in Fourier space as follows :

$$\delta n(\vec{r} - \vec{R}_i) = \sum_q \delta n^i_{\vec{q}} \; e^{i\vec{q}\cdot\vec{r}} \quad \text{and} \quad \frac{1}{|\vec{r} - \vec{r}'|} = \sum_q \frac{4\pi}{q^2 \Omega} \; e^{i\vec{q}\cdot |\vec{r}-\vec{r}'|}$$

where Ω is the volume of the space containing $\vec{r}$ and $\vec{r}'$, the first term in the expression (22) becomes

$$-n_o \sum_{\vec{q} \; \vec{q}'} \frac{4\pi}{q^2 \Omega} \; \delta n^i_{\vec{q}} \int e^{i\vec{q}\cdot\vec{r}'} \; e^{i\vec{q}'\cdot(\vec{r}-\vec{r}')} \; d\vec{r} \; d\vec{r}'$$

$$= -n_o \sum_{\vec{q}} \frac{4\pi \; \delta n^i_{\vec{q}}}{q^2} \int e^{i\vec{q}\cdot\vec{r}} \; d\vec{r}$$

$$= -4\pi \; n_o \Omega \lim_{\vec{q} \to 0} \left(\frac{\delta n^i_{\vec{q}}}{q^2} \right)$$

$$= + \frac{2\pi n_o}{3} \int r^2 \delta n(\vec{r}) \; d\vec{r} \quad (23)$$

The second term of the same expression is

$$\Omega \sum_{\vec{q}} \frac{(\delta n^i_{\vec{q}} \; \delta n^i_{-\vec{q}})}{q^2} \quad (24)$$

Now we can write the expression for the one centre term as

$$\Delta U_I = -\frac{2}{\pi} \sum_{\ell} (2\ell+1) \int_0^{\varepsilon_F} \delta_\ell(\varepsilon)d\varepsilon + \int (\delta\varepsilon'_{xc}-\delta\mu'_{xc})[n_0+\delta n(\vec{r})]d\vec{r}$$

$$+ \frac{2\pi n_0}{3} \int r^2 \delta n(\vec{r})d\vec{r} - \Omega \sum_q \frac{(\delta n_{\vec{q}} \delta n_{-\vec{q}})}{q^2} \qquad (25)$$

The two centre terms ΔU_{II} can be estimated from the functional relation of kinetic, exchange and correlation energies

$$T[n_0 + \Delta n(\vec{r})] + E_{xc}[n_0 + \Delta n(\vec{r})] = T[n_0] + E_{xc}[n_0] +$$

$$\frac{\delta(T+E_{xc})}{\partial n} \bigg|_{n=n_0} \int \Delta n(\vec{r})d\vec{r}$$

$$+ \tfrac{1}{2} \int \Delta n(\vec{r}) \Delta n(r') \frac{\partial^2(T+E_{xc})}{\partial n(\vec{r})\partial n(\vec{r}')} \bigg|_{n=n_0} d\vec{r}\,d\vec{r}' \qquad (26)$$

As shown by Kohn and Sham[23] one can write

$$\frac{\partial(T+E_{xc})}{\partial n(\vec{r})\partial n(\vec{r}')} \bigg|_{n(\vec{r})=n_0} = K(\vec{r}-\vec{r}') = \frac{1}{\Omega} \sum_q K_q e^{-i\vec{q}\cdot(\vec{r}-\vec{r}')}$$

where K is the response function and $K_q = \frac{2\pi}{q^2} \frac{1}{\varepsilon_q -1}$ is the dielectric function and $\Delta n(r) = \sum_i \delta n(\vec{r}-\vec{R}_i)$ is a periodic function having the lattice periodicity.

From eqns. (18) and (26) we can collect the two centre terms to find out ΔU_{II} as

$$\Delta U_{II} = \int \delta n(\vec{r}-\vec{R}_i)\delta n(\vec{r}-\vec{R}_j)K(r-r')d\vec{r}\,d\vec{r}'$$

$$+ \tfrac{1}{2} \int \frac{\delta n(\vec{r}-\vec{R}_i)\,\delta n(\vec{r}'-\vec{R}_j)}{|\vec{r}-\vec{r}'|} d\vec{r}\,d\vec{r}' \qquad (27)$$

Writing δn and K in terms of Fourier series expansion

$$\delta n(\vec{r}-\vec{R}_i) = \sum_{\vec{q}} \delta n_{\vec{q}} \, e^{i\vec{q}\cdot(\vec{r}-\vec{R}_i)}$$

and

$$K(\vec{r}-\vec{r}') = \sum_{\vec{q}} K_q \, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}')}$$

We get,

$$\Delta U = \sum_q \frac{|\delta n_{\vec{q}}|}{2} \frac{4\pi}{\vec{q}^2} (1 + \frac{1}{\varepsilon_{\vec{q}}-1}) \, e^{i\vec{q}\cdot(\vec{R}_i-\vec{R}_j)} \qquad (28)$$

The contribution of this term to the ground state energy can be written following eqn. (17), as

$$\sum_{\substack{i,j \\ i \neq j}} \Delta U_{II} = \tfrac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \phi_{ij}$$

where $\hat{\phi}_{ij} = \phi(|\vec{R}_i-\vec{R}_j|) = \sum_{\vec{q}} \frac{|\delta n_{\vec{q}}|^2}{\vec{q}^2} (\frac{4\pi}{1-\varepsilon_{\vec{q}}-1}) e^{i\vec{q}\cdot|\vec{R}\,\vec{R}_j|}$

This can be looked upon as the interatomic potential between the pseudo-atoms at lattice sites i and j. This expression unlike its counterpart in the pseudo-potential theory, does not use the linear response approximation, i.e. the assumption that the electron gas responds linearly to the potential V_{ext}^i. The treatment is exact apart from the local density approximation for the exchange and correlation contribution to the potential, assumption of a spherically symmetric potential, and the neglect of terms in density arising from two centre interference, and neglect of three and higher centre contributions to E_g.

In the treatment of Dagens[9], a neutralizing auxiliary charge distribution $n_A(\vec{r})$ at each lattice site is postulated. This has a Gaussian or similar form, and $\int n_A(\vec{r}) d\vec{r} = Z_A$. The effect of the difference between $n_A(\vec{r})$ and the uniform distribution n_o spread over the Wigner-Seitz cell is treated in perturbation. Assumption of a neutral auxiliary pseudo-atom is unnecessary as shown above; it is a source of arbitrariness since the distribution $n_A(\vec{r})$ is not unique. Ball[47] has used n_o over the WS cell directly, as we have, but costs his theory in the form of pseudo-potential perturbation theory. We have shown above how the density functional formalism can be directly used, once the pseudo-atom charge density is known, to calculate the energy change due to the coupling of pseudo-atoms via the electron gas. Since the $\delta n(\vec{r} - \vec{R})$'s are localized around their respective cells and since the coupling kernel $K(\vec{r} - \vec{r}')$ is short ranged ($|\vec{r} - \vec{r}'| \sim k_F^{-1}$), the two centre term can be expected to be small.

The advantage of this method is that it is not necessary to use a pseudo-potential. The two centre or inter-atomic term being small i.e. of the order of 4 percent of one centre term the method is rapidly convergent. On the question of whether it can be applied to transition metals

or not good prospects appear to be there for the following reasons: (a) The transition metals also form close packed, non-directionally bonded structures, (b) The energy difference between bcc, fcc and hcp structures are small confirming non-directional bonding (c) The inter-atomic potentials derived from the structure factor data appear to be quite strong in transition metals indicating stronger intercell coupling but again it might still be small as the ratio of this to the cohesive energy may be as small as in simple metals(transition metal cohesive energies are much larger than in simple metals the ratio of melting temperature to cohesive energy ($T_m/E_{coh.}$) seems to be the same for say the alkali metals, and noble and transition metals).

The identification of the two centre term with the interatomic potential implies physically that each ion carries its neutralising Wigner-Seitz cell of electrons around it. While this is acceptable when the ions are in lattice positions, in a liquid or vibrating solid this premise has to be examined. If this is correct there also then we have a simple method for calculating the interatomic potentials which appears to be valid for transition metals as well.

Using a spin density functional one can try to find the condition for the pseudo-atom to be magnetic. This also will

give the spin density oscillations, T_c, hyperfine fields etc. This area is still totally unexplored through this method.

5.3 The Heat of Solution of Alloys: Simple Alloys :

Suppose in a system one of the lattice site i has ion A with charge Z_A whereas all the other sites are occupied by ions B with charge Z_B. The energy of the system can be written as

$$E = E_A^{(B)} + (N-1) E_B + E_{AB} \qquad (30)$$

where $E_A^{(B)}$ is the energy of the pseudoatom A as it exists in the alloy, E_B is the energy of a single pseudoatom B in pure B and E_{AB} is the interaction energy between pseudoatom A and the surrounding B pseudoatoms. If similary define E_A as the energy of a single pseudoatom in pure A, the heat of solution per atom of A can be written as

$$\Delta \bar{\bar{H}} = E - E_A - (N-1) E_B = E_A^{(B)} - E_A + \Delta E_{AB} \qquad (31)$$

Now let us try to write the total energy of the system in the form of eqn. (30). Following eqn. (17) if we write the total energy as

$$E = E[n_o] + \Delta U_I + \Delta U_{II} \qquad (32)$$

with n_o as the average density of electrons in pure B and

ΔU_I and ΔU_{II} as one centre and two centre terms respectively, we can express $E[n_o]$ as

$$E[n_o] = \{ T[n_o] + E_{xc}[n_o] \}_B^{N-1} + \{ T[n_o] + E_{xc}[n_o] \}_A^1 +$$

$$(N-1) E_B^{es} + E_B^{es} + \tfrac{1}{2} \sum_{1 \neq 0} \frac{\Delta Z \, Z_B}{|\vec{R}_1|}$$

$$= (E_o)_B^{N-1} + (E_o)_B^1 + \tfrac{1}{2} \sum_{1 \neq 0} \frac{Z_B \Delta Z}{|\vec{R}_1|}$$

where the superscripts like N-1, 1 indicates the number of pseudoatoms, the subscripts identify the cells, E_B^{es} is the electrostatic energy of pseudoatom B as in the pure state. Similarly we can write ΔU_I as

$$\Delta U_I = \frac{2}{\pi} \sum_{j \epsilon B, 1} (21+1) \int_0^{\epsilon_F} \epsilon \, \frac{d\delta_1^j(\epsilon)}{d\epsilon} \, d\epsilon$$

$$+ \sum_{j \epsilon B} \int (\delta \epsilon_{xc}^j - \delta \mu_{xc}^j)[n_o + \delta n^B(\vec{r} - \vec{R}_j)] d\vec{r}$$

$$+ \sum_{j \epsilon B} \int \frac{\delta n^B(\vec{r} - \vec{R}_j) \, n_o \Theta(|\vec{r}'| - r_{BB})}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$- \tfrac{1}{2} \sum_{j \epsilon B} \iint \frac{\delta n^B(\vec{r} - \vec{R}_j) \delta_n^B(\vec{r}' - \vec{R}_j)}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$+ \frac{2}{\pi} \sum_1 (21+1) \int_0^{\epsilon_F} \epsilon \, \frac{d\delta_1^A(\epsilon)}{d\epsilon} \, d\epsilon$$

$$+ \int (\delta \epsilon_{xc}^A - \delta \mu_{xc}^A)[n_o + \delta n^A(\vec{r})] d\vec{r}$$

$$+ \int \frac{\delta n_o^A(\vec{r}) \, n_o \theta(|\vec{r}'| - R_B)}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$- \frac{1}{2} \iint \frac{\delta n_i^A(\vec{r}) \, \delta n_i^A(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$= (N-1) \, \Delta U_I^B + \Delta U_I^A \tag{33}$$

where δn^B is the deviation of charge density from the uniform n_o for pure B and δn^A is the deviation from n_o in the Wigner–Seitz cell of solute in the alloy. The two centre term also can be evaluated in the same way to give

$$\Delta U_{II} = \sum_{\substack{i,j \in B \\ i \neq j}} \int V_{ext}^B(\vec{r} - \vec{R}_i) \delta n^B(\vec{r} - \vec{R}_j) d\vec{r} + \sum_{\substack{i,j \\ i \neq j}} \iint \delta n^B(\vec{r} - \vec{R}_i) \delta n^B(\vec{r} - \vec{R}_j) d\vec{r} d\vec{r}'$$

$$[\tfrac{1}{2} \frac{1}{|\vec{r} - \vec{r}'|} + K(\vec{r} - \vec{r}')] + \sum_{j \in B} [V_{ext}^B(\vec{r} - \vec{R}_j)\delta n^A(\vec{r}) + V_{ext}^A(\vec{r})\delta n^B(\vec{r} - \vec{R}_j)] d\vec{r}$$

$$+ \sum_{j \in B} \iint \delta n^A(\vec{r})\delta n^B(\vec{r}' - \vec{R}_j)[\frac{1}{|\vec{r} - \vec{r}'|} + 2K(\vec{r} - \vec{r}')] d\vec{r} \, d\vec{r}' + \sum_{j \in B} \frac{Z_B \Delta Z}{|\vec{R}_j|} \tag{34}$$

The first two terms of eqn. (34) can be written as

$$\sum_{i,j} \int V_{ext}^B(\vec{r} - \vec{R}_i)\delta n^B(\vec{r} - \vec{R}_j) d\vec{r} - 2 \sum_{j \neq 0} V^B(\vec{r})\delta n^B(\vec{r} - \vec{R}_j) d\vec{r}$$

$$+ \sum_{ij} \int \delta n^B(\vec{r} - \vec{R}_i)\delta n^B(\vec{r} - \vec{R}_j)[\frac{1}{2|\vec{r} - \vec{r}'|} + K(\vec{r} - \vec{r}')] \, d\vec{r} \, d\vec{r}'$$

$$-2 \sum_{j \neq 0} \int \delta n^B(\vec{r}) \, \delta n^B(\vec{r} - \vec{R}_j)[\frac{1}{2|\vec{r} - \vec{r}'|} + K(\vec{r} - \vec{r}')] d\vec{r} \, d\vec{r}' \tag{34a}$$

This can be better understood in terms of bonds because the difference in the number of B-B bonds if one site is occupied by A with that if it had been occupied by B is $\frac{N(N-1)}{2} - \frac{(N-1)(N-2)}{2} = \frac{2}{N} \frac{(N(N-1)}{2}$. So, if E^{BB} is the bond energy per atom in pure B the expression (34a) can be written as

$$N \, E^{BB} - 2 \, E^{BB} = (N-1)E_{BB} - E_{BB}$$

The rest of the terms in eqn. (34) can be written as

$$E_{BA} = \sum_{j \neq 0} \int \delta n^B(\vec{r} - \vec{R}_j)[V^A_{ext}(\vec{r}) + \int \frac{\delta n^A(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}']d\vec{r} +$$

$$+ \sum_{j \neq 0} [\int - \frac{\delta n^A(\vec{r}) \, Z_B}{|\vec{r} - \vec{R}_j|} d\vec{r}]$$

$$+ 2 \sum_{j \neq 0} [\delta n^A(\vec{r}) \, \delta n^B(\vec{r} - \vec{R}_j) \, K(\vec{r} - \vec{r}') \, d\vec{r} \, d\vec{r}' + \frac{\Delta Z \cdot Z_B}{|\vec{R}_j|}] \quad (34b)$$

The evaluation of this type of terms have been discussed in the pure case and the only difference here is $\int \delta n^A(\vec{r})d\vec{r} = Z_A - Z_B = \Delta Z$. The contribution from the two centre terms can be written in terms of eqn. 34(a) and (b) as

$$\Delta E_{AB} = E_{AB} - E_{BB} \qquad (35)$$

So collecting all the one centre, two centre terms together we can write the final expression for the heat of solution per atom of solute as

$$\Delta \bar{H} = \frac{2}{\pi} \sum_{1} (2l+1) \int_{0}^{\varepsilon_F} \varepsilon \varepsilon \left(\frac{d\delta_1^A(\varepsilon)}{d\varepsilon}\right) d\varepsilon + \int (\delta\varepsilon_{xc}^A - \delta\mu_{xc}^A)[n_0 + \delta n^A(\vec{r})] d\vec{r}$$

$$+ \int \frac{\delta n^A(\vec{r}) \, n_0 \theta(\vec{r}'R_B)}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}' - \frac{1}{2} \int \frac{\delta n^A(\vec{r}) \, \delta n^A(\vec{r}')}{|\vec{r} - \vec{r}'|} \, d\vec{r} \, d\vec{r}'$$

$$+ E_{AB} + T[n_0] + E_{xc}[n_0] + (E_B^{e.s})_A - E_A \qquad \qquad (36)$$

The calculation of one centre terms involved in the eqn. (36) can be done in the Fourier space as detailed in the discussion for the pure case.

5.4 Calculation and Results

In the present section we will describe the numerical methods ·followed to solve the Schrodinger equation like Kohn-Sham eqn. (11) and present the result for the phase shift and $\delta n(\vec{r})$ in Al, Mg and Al-Mg alloy. These results are non-self consistent and the problems of self-consistency will be discussed in the context of these results. From the δ 's and the $\delta n(\vec{r})$'s we evaluate the cohesive energies for Al, Mg and the heat of solution of the Al-Mg alloy by eqns. (17), (33) respectively. These results will also be presented here.

(i) The Solution of the KS-equation :

The KS equation poses an initial value problem for a linear second order differential equation and there are several methods to solve it. But to follow any numerical

method for its solution the first task is to divide real space into a mesh. Then the equation is solved at each point of thie mesh.

For the case of atoms, the radial wave f_n is oscillatory at small and medium values of r, and exponentially damped at large values of r. Our case is quite different. In the beginning (near origin) we have an exponentially damped radial wave function and at large r it is free electron like. The charge density (rather the difference in charge density from the initial uniform distribution i.e. $\delta n(\vec{r})$ has oscillations through out. The determination of phase shifts requires accurate values for the radial wave function at large r where only can it be well approximated by its asymptotic form.

From these considerations we can see that our choice need be different from that of Herman and Skillman[45]

for the atomic case. Our mesh is uniformly spaced at distances of Δr and the KS equation is solved upto a distance of $\angle$ of R_T where the phase shift is determined by matching it with the asymptotic form. In general, smaller r and larger R_T give better results. But the limitation of the memory of the computer demands an optimum choice.

The method followed to solve the KS equation numerically is due to Numerov which is described in detail in the book by Hartree[49] . It runs as follows: for small r(i.e. the first two points on the mesh) the KS equation is solved analytically for a given potential and a given energy. Since the potential in the cases considered is highly positive near origin the solution will be in terms of modified spherical Bassel function (we use the condition that the radial wave function is finite at origin). After knowing the solution at the first two points of the mesh we start the outward integration procedure at each outward point involving the adjacent two inward points where the solution is already known (see the book by Hartree[49]). This was done by a modified version of the computer programme written by Hermann and Skillman[45] for the case of atoms.

Since we need the phase shifts for our purpose we had to incorporate this calculation in the above computer programme. The asymptotic form of a phase shifted radial wave function for the angular quantum no.1 is given by

$$\lim_{r \to large} R_{1k}(r) = \cos \delta_1 \, j_1(kr) - \sin \delta_1 n_1(kr) \qquad (37)$$

where j_1 and n_1 are the spherical Bessel and Neumann functions for a given 1 and the energy $E = k^2$ in the

Rydbergs. If we choose test radius R_T at sufficiently large r where the radial wave function has taken the form given by eqn. (37). The phase shift can be expressed as

$$\tan \delta_l = \frac{k j'_l(kR_T) - \gamma_l j_l(kR_T)}{k n'_l(kR_T) - \gamma_l n_l(kR_T)} \qquad (38)$$

where

$\gamma_l = \frac{1}{R_l} \frac{dR_l}{dr}$ can be found out from the numerical solution described in the last paragraph. j'_l and n'_l are derivatives of j_l and n_l with respect to r.

To choose an optimum mesh size Δr and test radius R_T, for a given potential we vary both these quantities Δr and R_T and study their effect on δ 's. Δr was varied from .01 to .08 a.u. and R_T was varied from $R_T = 4.0$ a.u. to 14.0 a.u. The δ_l's were found to be stable for $\Delta r = .05$ a.u. and $R_T = 6.0$ a.u. So, we choose for our calculations a mesh size $\Delta r = .04$ and determinie the phase shifts at $R_T = 8.0$ a.u.

After calculating the phase shifts we need to calculate the deviation $\delta n(\vec{r})$ from the starting distribution of the electrons (which we assume to be uniformly $\bar{n}$). $\delta n(\vec{r})$ is given by

$$\delta n(\vec{r}) \sum_{k < k_F} | \psi_k(\vec{r}) |^2 - \bar{n} . \qquad (39)$$

where the energy $E = k^2$ and k_F is the Fermi momentum. By expanding $\bar{n}$ in terms of spherical waves and writing $\psi_k(\vec{r})$ explicitly in terms of the radial wave functions one can rewrite the eqn. (39) as

$$\delta n(\vec{r}) = \frac{1}{\pi^2} \int_0^{k_F} k^2 \, dk \sum_{l=0}^{\infty} (2l+1) \{ [R_{lk}(r)]^2 - j_l^2(kr) \} \qquad (40)$$

Once R_{lk} values are calculated over the mesh, at each point the $\delta n(\vec{r})$ can be determined by eqn. (4. The normalisation of R_{lk} values obtained numerically can be done by comparing it with the eqn. (37) which is given in the normalised form.

With this $\delta n(\vec{r})$ given by eqn. (40) one can find the modified $n(\vec{r})$ (let us denote it by $n_1(r)$ of the system at the end of first cycle as given below

$$n_1(\vec{r}) = \bar{n} + \delta n(\vec{r})$$

This $n_1(\vec{r})$ can how be put in eqn. (16) to give the effective potential to be used in the next cycle to solve the KS equation. This way one can go on until the self-consistency is achieved. The final values of the $\delta_1(\varepsilon)$'s for the given energy ε and $\delta n(\vec{r})$ obtained self-consistently can be used to find out the cohesive energy of the pure metals and the heat of solution of alloys from eqns. (17) and (33) respectively.

The above calculation should give self-consistent

δ_1s which satisfy the Friedel sum rule.

$$\Delta Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \, \delta_l(\varepsilon_F) \qquad (41)$$

where ε_F is the Fermi energy of the system, $\Delta Z = 0$ for pure metals and equal to $Z_A - Z_B$ for the alloys, we can start from any form of initial $n(\vec{r})$, the self consistent solution will give the same final $n(\vec{r})$, and satisfy eqn. (41). But a better choice of initial $n(\vec{r})$ used in calculating V_{eff} will converge to the self consistent solution faster. Since we find from our experience with the parametric variational scheme that the uniform charge distribution gives a good approximation for the ground state charge density. Our initial charge density is taken to be uniform ($\bar{n}$) and to have the equilibrium value, i.e. to contain charge Z_A in a volume of rarius R_A. But with the Ashcroft empty core pseudopotential and this choice of initial $n(r)$ the Friedel sum rule is not satisfied. So, we vary the atomic radius R_A (which is equivalent to changing $\bar{n}$) until we can satisfy the Friedel sum rule given by eqn. (41). It is quite a standard procedure to start with an initial distribution which satisfy the Friedel Sum rule (Lang and Kohn[6], Popovic and Stott[46]).

To check the accuracy of our numerical scheme we find out the phase shifts for different l in absence of any

potential (i.e. $V_{eff}(r) = 0.$). This yields zero δ_1 upto sixth decimal place for $R_T = 4.0$ a.u. and upto eighth decimal place for $R_T = 12.0$ with $\Delta r = 0.04$ a.u. in both the cases.

The l-values are generally taken upto $l = 2$ which we also follow in our calculation. But to check the amount of error involved we have calculated the $l = 3$ contribution to the Friedel Sum rule given by eqn. (6) as $(\Delta Z)_3 = 14 \delta (\varepsilon_F)/\pi.$ It is found to be quite small (~ 0.0046) for a calculation with the empty core pseudopotential for magnesium. $(\Delta Z)_3$ is also found to decrease with decreasing uniform density $\bar{n}.$ The empty core model potential tends to pile up charge in the region $r_c < r < R_A$ and this tendency becomes more prominent with iteration. This defect of the model potential can be overcome by choosing a flatter, smoother potential such as a local version of Animalu-Abarenkov Heine potential.

With all the precautions mentioned above when the calculations were carried out taking an empty core model pseudopotential for the ion it was found that after one or two cycles of relatively moderate deviation the $\delta n(r)$ starts changing violently. Animalu-Abarenkov-Heine (AAH) model potential was used (i.e. $l = 0$ component is only taken)

in its place.The local AAH potential is (as described in Chapter 1) given by

$$V_{ion}(r) = \begin{array}{ll} - \; Z/r_c & \text{for } r < r_c \\ - \; Z/r & \text{for } r > r_c \end{array} \qquad (43)$$

The values of r_c was taken from Shaw's calculation. For Mg $r_c = 2.58$ and for Al $r_c = 2.15$.

The results For $r^2 \delta n(\vec{r})$ at the end of first cycle for Al, Mg and Al-Mg alloy are plotted in Fig. 5.1(a), 5.2(a) and 5.3(a) respectively. These also shows V(r) in Rydberes in the accompanying figures marked (b) for each of these $r^2 \delta n(r)$ plots. The $r^2 \delta n(\vec{r})$ curves for the pure elements show that some charges have either flown out (.23 for Al) or moved inside (.016 for Mg) the sphere of radius R_T. This may be due to the fact that the phase shifts are inaccurately calculated while satisfying the Friedel Sum rule. As a result we might expect that the estimate of the cohesive energy or the heat of solution from these non-self-consistent calculations will be in error. But still we go ahead with the calculations so as to convince ourselves about the practicability of the schemes proposed.

The complete procedure involves finding Eg as a function of n_0 and locating the minimum. That is, for a
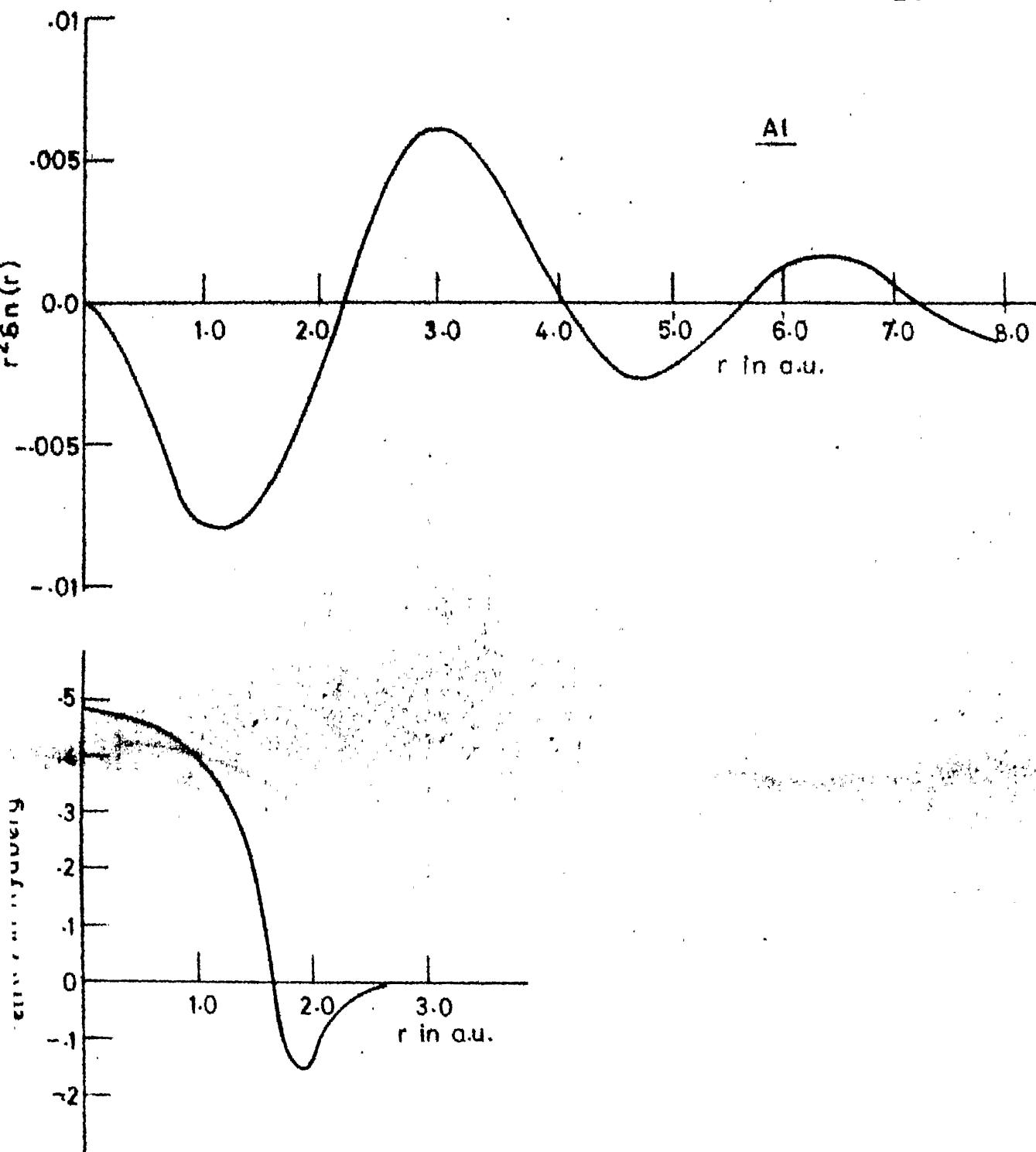
FIG 5.1 : VARIATION OF (a) DIFFERENCE BETWEEN TRUE CHARGE DENSITY
AND THAT OF UNIFORM ELECTRON GAS MODEL,$r^2\delta n(r)$ WITH
DISTANCE, r, FROM ORIGIN (b) EFFECTIVE POTENTIAL,
$V_{eff}(r)$, WITH DISTANCE, r, FOR ALUMINIUM.
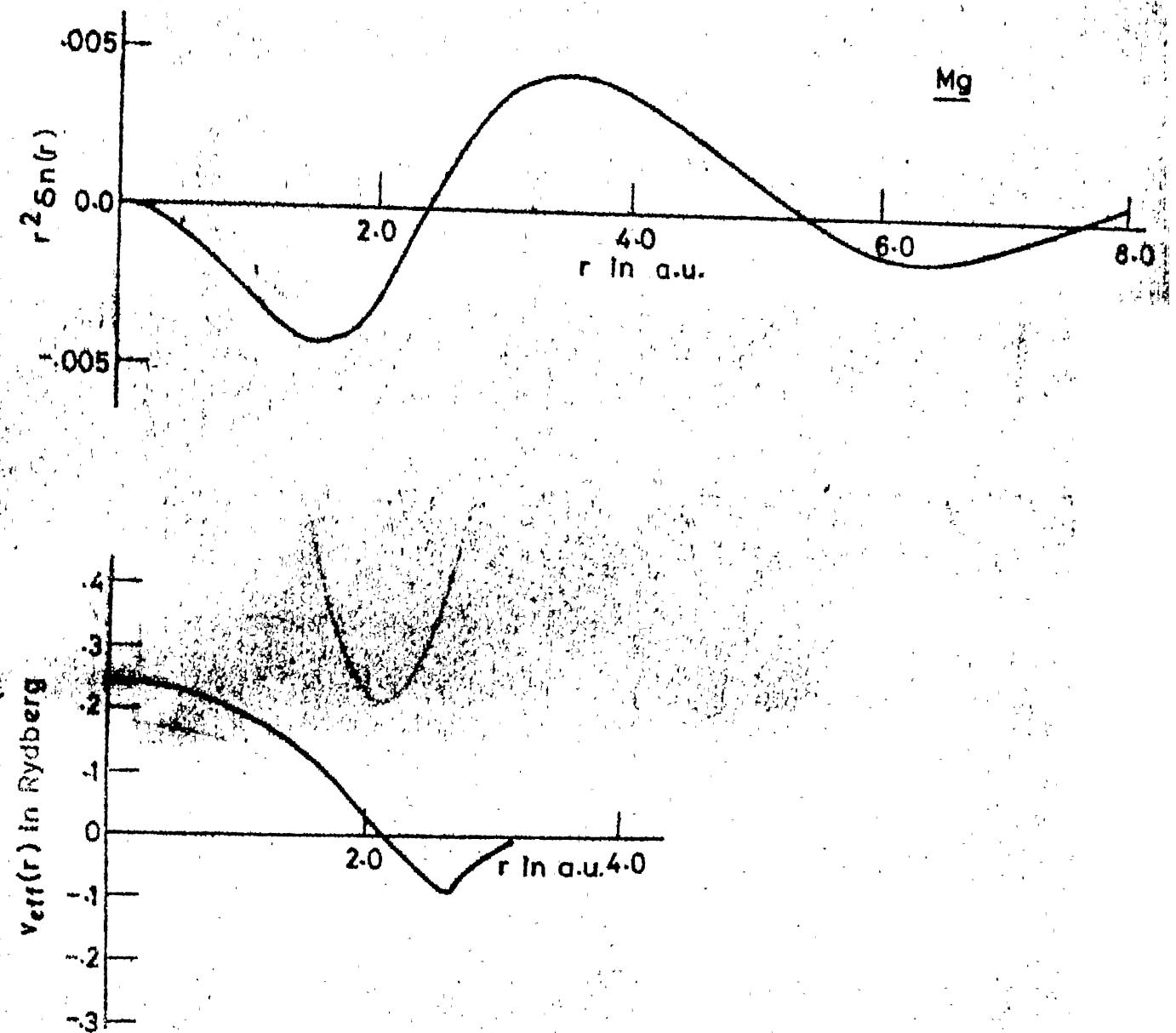
FIG 5.2 : VARIATION OF (a) DIFFERENCE BETWEEN TRUE CHARGE
DENSITY AND THAT OF UNIFORM ELECTRON GAS MODEL, r^2
$\delta n(r)$ WITH DISTANCE, r, FROM ORIGIN (b) EFFECTIVE
POTENTIAL, $V_{eff}(r)$, WITH DISTANCE, r, FOR
MAGNESIUM.
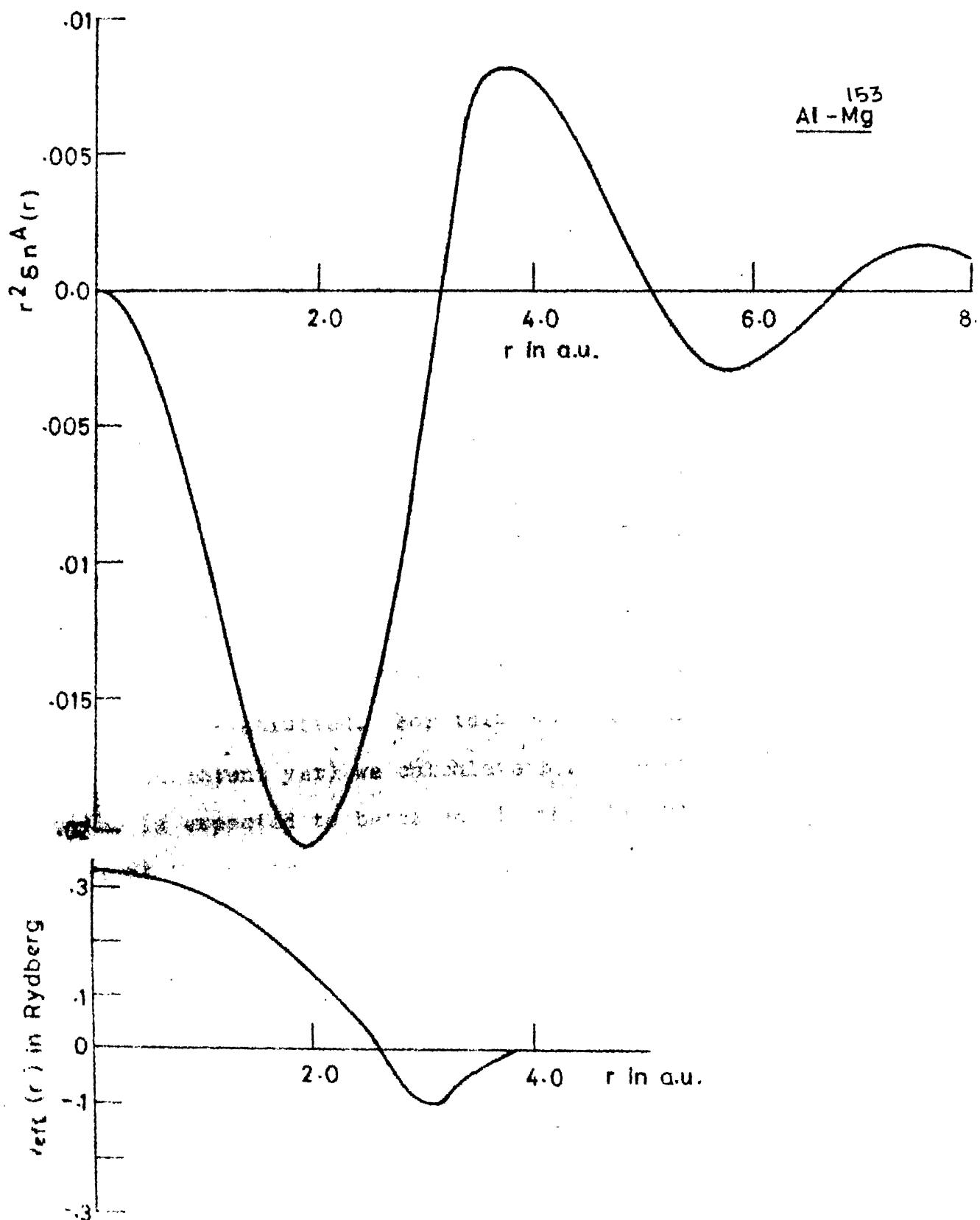
5.3 : VARIATION OF (a) DIFFERENCE POTENTIAL TYPE CHARGE DENSITY AND THE
OF ..... (b) IN URID.. ..... (AS MULTIPLE r^2 δ$n^A r$) WITH
D.... (a) FOR ... TAE SIZE (b) ... OF POTENTIAL OF SOLUTE
V.....), WI... .... FOR A...... ..... 153 Al ALLOY.

given n_0 (and hence lattice constant) we obtain the self consistent $\delta n(\vec{r})$ and the corresponding Eg. This is done for several values of n_0, the lowest value of E_g is cohesive energy and the corresponding n_0 is to be compared with the observed density. Further, in principle, the ion potential may be used directly (as discussed in Section 5.2); it need not be modelled by a pseudopotential. Unfortunately, since we have not solved the self-consistency problem, we have not done the complete cohesive energy calculation as above. For an n_0 value given by the experiment, we vary the initial potential as described above till the Friedel Sum Rule is satisfied. For this neutral configuration (not self consistent yet) we calculate E_g. The calculated value is expected to be close to the observed E_g since most of the contribution is from n_0.

Table 5.1 shows the phase shifts δ_i's for $l = 0$, 1 and 2 for Mg, Al and Al-Mg alloy. In the pure Al or Mg metal we find that although the phase shifts at ε_F satisfy the Friedel Sum Rule approximately still the $r^2 \delta n(\vec{r})$ curves plotted in Fig. 5.1(a) and 5.1(b) show an amount of charge flow (to or away from the origin. This can only result from an inaccurate calculation of phase-shift which involves derivative of R_l and hence is quite susceptible to error.

TABLE 5.1

Variation of Phase Shifts with Energy for Al, Mg and Al-Mg Alloys

No.(n)	Mg			Al			Al-Mg		
	$\delta_o(\varepsilon)$	$\delta_1(\varepsilon)$	$\delta_2(\varepsilon)$	$\delta_o(\varepsilon)$	$\delta(\varepsilon)$	$\delta(\varepsilon)$	$\delta_.(\varepsilon)$	$\delta(\varepsilon)$	$\delta_.(\varepsilon)$
1	.005	.001	.0000	.058	+.006	+.0000	.094	.001	.0001
2	.001	.004	.0001	.172	+.022	+.0002	.152	.002	.0007
3	-.010	.006	.0005	.138	+.044	+.0007	-.210	-.001	.0024
4	-.025	.009	.0009	-.021	+.074	+.0017	-.260	-.010	.0049
5	-.042	.013	.0014	-.096	+.082	+.0031	-.298	-.025	.0075
6	-.057	.017	.0017	-.144	+.101	+.0041	-.321	-.041	.0091
7	-.070	.019	.0026	-.189	+.105	+.0061	-.332	-.057	.0094
8	-.080	.020	.0039	-.221	+.109	+.0071	-.336	-.069	.0090
9	-.085	.021	.0036	-.338	+.111	+.0077	-.336	-.076	.0084

ε Correspondong to each n is given by $\varepsilon = n\varepsilon_F/9.0$ when ε_F is the Fermi-energy of the relevent system, i.e. Mg, Al or Al-Mg alloy.

Table 5.2 shows the estimated value of the different terms involved in the calculation of cohesive energy of pure metals by eqns. (24) and (25). Some of the terms which give positive values for Mg are found negative in the case of Al. This may be due to the fact that $r^2 \delta n(\vec{r})$ has positive deviation from zero in case of Mg while it is negative for Al. The comparison of the observed cohesive energy with the calculated one is good in view of the fact that Friedel Sum rule has not been satisfied. But the difference in the calculated and the observed cohesive energies of Aluminium is quite large. This may be due to again the flow of electrons away from the region of $r < R_T$. We see also that the charge oscillations are fairly prominent. We note that the contribution of n_o or the uniform part to the ground state energy is much larger than the residual one centre, and the two centre terms. The ratio is 170:3:0.5 for M_g and 381:1:0.2. Thus, as seen earlier, most of the cohesive energy is due to the uniform part of the electron gas density. The smallness of U , justifies our neglect of three and higher centre terms. The cohesive energies are close to the observed values.

Table 5.3 shows the calculation of the heat of solution for the Al-Mg alloy by eqn. (36).

TABLE 5.2

Values of Different Terms in Equation (25) and (26) for the Cohesive Energy Calculation

Eqn. (25) : U_i

		M_g	Al
1st term	:	-.008244	.093452
2nd term	:	+.018768	+.028366
3rd term	:	.017928	-.019492
4th term	:	-.000482	-.001156
U_i	=	.028170	.101171
Eqn. (26) : U_{ij}	=	.005414	.021417
		.033584	.122588
$E[n_o]$		-1.704676	-3.960880
Calculated cohesive energy		-1.671092	-3.838292
Observed cohesive energy		-1.784	-4.14

All the energy terms are expressed in rydbergs.

The first term is the change in the one electron energy. This is positive, as is the exchange and correlation term. The third term, representing the electrostatic interaction between the uniform electron distribution in the matrix with the charge deviation $\delta n(\vec{r})$ centred at the impurity is negative. This is because the $\delta n(\vec{r})$ is negative (there is one less electrons in the impurity cell centred pseudoatom, than in the host pseudoatom). The next term, being the negative of half the e.s. self energy of the distribution $\delta n(r)$, is also negative. The fifth term represents the electron gas mediated interaction between Mg and Al pseudo-atoms. This is, interestingly, attractive. To these, we add the uniform Al contribution and subtract the g.s.e. of Mg. The value we obtain is negative, but about three times larger than the observed value.

We cannot draw too many conclusions from this incom-plete and isolated result. There is every reason to believe, however, that if the self consistency problem is solved, the above Kohn Sham procedure would lead to a very good quantitative and qualitative understanding of cohesive energy of metals, and heat of solution of alloys. The method is free from the inadequacies of the variational procedure of Chapters 3 and 4. It requires no pseudopoten-tial, no assumption of form for $n(\vec{r})$. The approximations

TABLE 5.3

Calculation of the Heat of Solution of Al-M$_g$ Alloy
by eqn.(36)

Eqn. (36) : 1st term   :   .8975

           2nd term   :   .7372

           3rd term   :   -1.2140

           4th term   :   -.2321

           5th term   :   -.0783

           6th to 8th term :   -1.9567

           9th term   -1.6711

                          —————————

                       - .1753

               54.8 K cal/gm. atom

All the energy terms are in Rydberys

made seem (both on the basis of our calculations and self
consistent calculations of Dagens[9]   for alkali metals)
to introduce negligible errors, and to be well justified.
The various terms contributing to E_g can be physically inter-
preted, and the charge distribution is also obtained. We
expect to pursue this approach to a conclusion.

Chapter 6 .

Conclusion

We have described in this thesis an attempt to study properties of dilute simple metallic alloys using the density functional method. The properties of interest are heat of solution, charge transfer etc. We have shown how the density functional formalism can be adapted to the case of dilute alloy, i.e. a metal atom A embedded in a matrix B. The two commonly used versions of the density functional formalism are variational parametrization of the density, and use of the variational principle to obtain a Schrodinger like equation from this the wave functions ψ , and the density $n(\vec{r})$ are calculated. The latter determines the potential, and there is a self-consistency problem to be solved. Once the density is known, the ground state energy E_g and thence the heat of solution can be obtained by using a well known functional form for E_g as a functional of $n(\vec{r})$.

In recent years, both methods have been applied with great success to the problem of metallic surfaces. Clearly, the variational parametrization method, though computationally simpler, is limited by the choise of variational functions possible with a few parameters. The latter or Kohn Sham method gives more realistic $n(\vec{r})$, and is much more

powerful. It has recently been applied to the chemisorption problem (calculation of chemisorption energy of a charge Z as a function of distance d from the surface) by Lang and co-workers[48] again with great success.

Initially, the parametric variational method was used by us on account of its simplicity. The results obtained can be viewed in two different ways: either in terms of how well they relate to real metals, or as studies of systematic trends in stable model metallic systems similar to real metals. The results obtained by us do not always describe with reliability and quantitative accuracy, the observed heats of solution of real metals. There are many good reasons for this. The most important is the fact that the heat of solution is a very small quantity, typically $\leq$ 1 percent of the cohesive energy. Thus errors which do not matter in cohesive energy calculations can be important for heat of solution. For example, the periodic component of the density, though large, contributes very little to the pure metal cohesive energy. However, its presence may aid or hinder the process of charge adjustment in the alloying region, and may thus influence the heat of solution. It is difficult to include this effect in the parametric variational method without complicating it enormously. In the one place we have tried to include it (Ml - I2 system

see Chapter 4 Section 4), the effect is sizeable, and in the right direction. We have also had to use a pseudopotential to represent the ion (this limits the applicability of the method to simple nontransition metals), and have used a local density functional formalism with a gradient term.

For $MZ_B - IZ_A$ systems with $Z_A < Z_B$, we find alloying with charge transfer. By varying the core radius of the pseudo-potential, the host or impurity equilibrium size can be varied. The heat of solution has been studied as a function of the host or impurity radius, and systematic trends have been found (these are discussed in Chapter 4). We have also attempted to analyze these trends in terms of concepts commonly used in alloy theory, namely size and electrochemical factors. The first problem is of quantitative definition of these. We have attempted some definition. However, though the latter can be identified with the electrochemical potential μ which has a precise definition, its accurate calculation has not been possible. Two estimates are presented. Using these, we have tried to correlate charge transfer ΔQ and heat of solu-tion (except for the size factor term) with $\mu_B - \mu_A$. Though there is a definite correlation, it is not as simple as suggested by 'small deviation theories. In addition, to the uncertainty in μ , a contributory cause could be the fact that charge transfer takes place well inside the

impurity WS cell, and not on its surface or over a large
volume. Thus, local effects may be significant and over-
all quantities like μ may not be the only important factors.

We have also presented, inter alia, calculations of
for the g.s.e. of a pure simple metal in the local density
approximation in which the periodic component is not calcu-
lated in perturbation theory. These calculations show the
periodic density component to be substantial but its contri-
bution to g.s.e. to be small.

In Chapter 5, we describe how the Kohn Sham method can
be reformulated as a weakly interacting pseudoatom model for
pure metals and dilute alloys. As mentioned earlier, in
this method, no assumption is made about the form of $n(\vec{r})$
which is obtained from solutions of a Schrodinger like equa-
tion. This method, as formulated here, can be expected to
lead to reliable values for alloy parameters, as well as
to qualitative understanding of the values. We have not been
able to solve the self-consistency problem here, and so
present only preliminary results of a single calculation,
for an Al-Mg alloy.

BIBLIOGRAPHY

(1) W. Hume-Rothery, J. Inst. Metals 35, 295(1926); W. Hume-Rothery and G.V. Raynor, Proc. Roy, Soc.(London) A174, 471(1940).

(2) L. Pauling, 'The Nature of the Chemical Bond', Cornell Univ. Press, Ithaca, New York (1960).

(3) C.H. Hodges and M.J. Stott, Phil. Mag, 26, 375, 1972.

(4) N.F. Mott and H. Jones, 'The Theory and Properties of Metals and Alloys', Oxford Univ. Press (Clarendon), London and New York (1936).

(5) J. Friedel, Advan. Phys. 3, 446(1954).

(6) N.D. Lang and W. Kohn, Phys. Rev. B1, 4555(1970); ibid. B3, 1215(1971).

(7) J.E. Inglesfied, Acta Met. 17, 1395(1969); J. Phys. C (Solid St. Phys.), 2, 1285(1969).

(8) A.R. Miedema, F.R. deBoer and P.F. deChatel, J. Phys. F: Metal Phys. 3, 1558 (1973); A.R. Miedema, R. Boom and F.R. deBoer, in 'Crystal Structure and Chemical Bonding in Inorganic Chemistry', (Eds: C.J.M. Rooymans and A. Rabenau), p. 163, North Holland, Netherlands (1975).

(9) L. Dagens, J.de Physique, 34, 879 (1973).

(10) W. Hume-Rothery, in 'Phase Stability in Metals and Alloys', (Eds. P.S. Rudman et. al.) P.3, McGraw-Hill, New York (1966).

(11) W. Hume-Rothery and D.J. Roafe, Phil. Mag. 6, 55 (1961).

(12) A. Blandin, in 'Phase Stability in Metals and Alloys', (Eds. P.S. Rudman et. al), p. 115, McGraw-Hill, New York (1966).

(13) G.A. Rooke, in 'Soft X-Ray Band Spectra', (Ed. D.J. Fabian), Academic Press, New York (1968).

(14) V. Heine and D. Weaire, 'Solid State Phys. 24, 249 (1970).

(15) L. Dagens, M. Rasolt and R. Taylor, Phys. Rev. B11, 2726 (1975).

(16) R.A. Johnson, in 'Interatomic Potentials and Simulation of Lattice Defects', (Eds: P.C. Gehlen et. al.), p. 89, Plenum, New York (1972).

(17) W.H. Harrison, 'Pseudopotentials in the Theory of Metals', Benjamin, New York (1966).

(18) W.H. Harrison, in 'Interatomic Potentials and Simulation of Lattice Defects', (Eds. P.C. Gehlen et. al.), p. 89, Plenum, New York (1972).

(19) N.W. Ashcroft, in 'Interatomic Potentials, and Simulation of Lattice Defects', (Eds: P.C. Gehlen et. al.), p. 89, Plenum, New York. (1972).

(20) J.R. Smith, Phys. Rev. $\underline{181}$, 522 (1969).

(21) P. Hohenberg and W. Kohn, Phys. Rev. $\underline{136}$, B864 (1964).

(22) T.L. Gilbert, Phys. Rev. $\underline{B12}$, 2111 (1975).

(23) W. Kohn and L.J. Sham, Phys. Rev. $\underline{140}$, $\underline{A1133}$ (1965).

(24) A.K. Rajagopal and S. Ray, Phys. Rev. $\underline{B12}$, 3129 (1975); M. Rasolt and D.J.W. Geldart, Solid. St. Commun. $\underline{18}$, 549 (1976); L. Kleinman, Phys. Rev. $\underline{B10}$, 2221 (1974); L.J. Sham, in 'Computational Methods in Band Theory', (Eds. P.J. Marcus et. al), p. 458, Plenum, New-York, (1971).

(25) S.K. Ma and K.A. Brueckner, Phys. Rev. $\underline{165}$, 19 (1968).

(26) B.Y. Tong and L.J. Sham, Phys. Rev. $\underline{144}$, 1 (1966).

(27) R.G. Gordon and Y.S. Kim, J. Chem. Phys. $\underline{56}$, 3122 (1972).

(28) E.P. Wigner, Phys. Rev. $\underline{46}$, 1002 (1934).

(29) O. Gunnarson, B.I. Lundqvist and S. Lundqvist, Solid. St. Commun. $\underline{11}$, 149 (1972).

(30) P. Nozieres and D. Pines, Phys. Rev. $\underline{111}$, 442 (1958).

(31) Von Weizsacker, Z. Physik. $\underline{96}$, 431 (1935).

(32) W. Jones and W.H. Young, J. Phys. $\underline{C4}$, 1322 (1971).

(33) C.H. Hodges, Can. J. Phys. $\underline{51}$, 1428 (1973).

(34) W.P. Wang, R.G. Parr, D.R. Murphy and G.A. Henderson, Chem. Phys. Letters $\underline{43}$, 409 (1976).

(35) J.F. Janak, Phys. Rev. $\underline{B9}$, 3985 (1974); J.F. Janak, V.L. Moruzzi and A.R. Williams, Phys. Rev. $\underline{B12}$, 1257 (1975).

(36) V. Heine, in 'Physics of Metals', Vol. 1, Electrons (Ed. J.M.Ziman), Chapter 1, Cambridge Univ. Press, London and New York (1968).

(37) L. Hedin and S. Lundqvist, Solid State Phys. $\underline{23}$, (1969).

(38) G.G. Robinson and P.F. deChatel, J. Phys. $\underline{F5}$, 1502 (1975).

(39) N.W. Ashcroft and D.C. Langreth, Phys. Rev. $\underline{155}$, 682 (1967); ibid. $\underline{159}$, 500(1967); S.P. Singh and W.H. Young, J. Phys. $\underline{F2}$, 72(1972).

(40) D. Weaire, Unpublished quoted in Ref.(36).

(41) R. Hultgren, R.L. Orr, P.D. Anderson and K.K. Kelley, 'Selected Values of Thermodynamic Properties of Metals and Alloys', Wiley, New York (1963).

(42) F. Seitz, 'The Modern Theory of Solids', McGraw-Hill, New York, (1940).

(43) J.M. Ziman, Adv. Phys. $\underline{13}$, 89(1964).

(44) N.H. March and A.M. Murray, Phys. Rev. $\underline{120}$, 830 (1960); Proc. Roy. Soc. $\underline{A261}$, 119(1961).

(45) F. Herman and S. Skillman, 'Atomic Structure Calculations', Prentice-Hall, New Jersey (1963).

(46) Z.D. Popovic and M.J. Stott, Phys. Rev. $\underline{B13}$, 590(1976).

(47) M.A. Ball, J. Phys. $\underline{C2}$, 1248 (1969).

(48) N.D. Lang and A.R. Williams, Phys. Rev. Lett. $\underline{34}$, 531 (1975).

(49) D.R. Hartree, 'The Calculation of Atomic Structure', Wiley New York (1957).

Gradient expansion in the density functional approach to an inhomogeneous electron system

A. K. Rajagopal*

Center for Theoretical Studies, Indian Institute of Science, Bangalore 560012, India

S. Ray

National Aeronautical Laboratory, Bangalore 560017, India

(Received 25 November 1974)

The linearized integral equation obeyed by the irreducible vertex function associated with the density fluctuations is solved *exactly* up to second power in the wave vector. This is used to compute the static polarizability of the homogeneous electron system up to this order. It determines the gradient expansion coefficient in the density-functional formalism for the inhomogeneous electron system. The result is compared with existing approximate caclulations. The method of solution is applicable to irreducible vertex functions which appear in the determination of other correlation functions of the homogeneous systems. Our gradient term vanishes for both extreme high- and low-density regions, unlike the results of Kleinman and Sham.

I. INTRODUCTION

Almost a decade ago, one of us[1] developed methods of investigating the integral equation obeyed by an irreducible vertex function $\Gamma_{\uparrow\downarrow}(k;q)$ associated with the transverse spin susceptibility of an itinerant magnetic electron system. In the long-wavelength limit $q \to 0$, it was found that one may expand this vertex function in a power series in the wave vector, the coefficients of each power of which is a spherical harmonic expansion. In this way, the q^2 coefficient of the spin-wave dispersion is found to be an integral over $\Gamma_{10}^{(1)}(k)$, where the superscript indicates the coefficients of q in the $\Gamma_{\uparrow\downarrow}(k;q)$ expansion and the subscripts 10 mean the p-wave part with zero projection in the spherical harmonic expansion. It was then found that $\Gamma_{10}^{(1)}(k)$ obeys a linear integral equation which in turn was solved by a variational method, since a series solution in k of this equation was not found satisfactory. In this manner, the effects of interactions (including all renormalizations) among the electrons are taken into account almost completely within the scheme of the linearized-vertex-function formalism. To investigate the spin-density-wave (SDW) instability of this system, the solution of the static part of this same vertex equation for finite wave vectors is required. To examine this, we developed a variational method for $\Gamma_{\uparrow\downarrow}(k;q)$ directly and deduced from this a simple criterion for the SDW instability. The latter method was found very powerful in dealing with other vertex functions, and the author with his collaborators has examined other properties of the interacting electron system,[2,3] as well as its relationship with other methods such as moment-conserving schemes.[4,5]

In the density-functional approach to the inhomogeneous electron systems,[6-9] one finds that the better the knowledge of various correlation functions,[9] the better the description of the inhomogeneous sys-

tem. For instance, in Ref. 9, we used the Yukawa interaction model in the limit of large screening to deduce the spin splitting of energy bands in ferromagnets. In the paramagnetic case, in particular, Sham[10] has given a calculation of the static density-correlation function up to q^2 terms by solving the integral equation obeyed by the associated irreducible vertex function by one iteration. The purpose of this paper is to use the methods of Ref. 1 to determine the same quantity that Sham computed both by an exact solution of the vertex equation and by the variational method for which the general expression for all q for the quantity of interest already exists.[3] In contrast to the spin-wave calculation,. *it is found here that the vertex equation can be solved exactly in this limit.* All the integrals appearing in the theory can be done generally for a wide class of static interaction potentials. The detailed calculation for the Yukawa potential is derived from the general expressions. This therefore serves to determine how good the simple variational answer is to this order, as well as derive an exact expression for the coefficient of the square of the gradient of the density in the theory of the inhomogeneous electron system. Kleinman[11] has very recently developed a solution to the vertex equation to this order. He has criticized Sham's[10] work in the light of the results he has derived. We will here make a critical assessment of the situation.

In Sec. II, we give only a brief description of the solution to the vertex equation appropriate to the problem at hand. Elsewhere[12] we will give a complete account of this method and its application to other properties of the system. In Sec. III, the variational solution[3] is given to this order. The results are compared with each other in Sec. IV. In Sec. V, we specialize the results for the Yukawa interaction model, and we give a critical assessment of these expressions in relation to the works
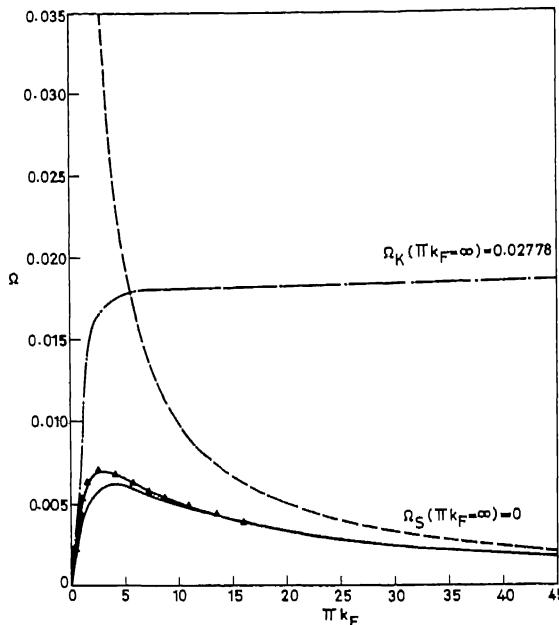
FIG. 1. Graph of Ω as a function of πk_F in Hartree units; Sham's: dashed curve; Kleinman's: dot-dashed curve; exact, Thomas-Fermi: solid-triangle curve; exact, self-consistent: solid-line curve.

of Sham[10] and Kleinman.[11] In this section, we also point out the adequacy of the schemes for calculating the screening parameter in the Yukawa model.[13] This is because with a pure Coulomb potential for the electron interactions, there is a divergence characteristic of the long-range nature of this potential.[10,11] A standard way to handle this is to introduce a screened Coulomb potential instead; if the screening is treated as a density-independent parameter, in the limit of it becoming zero, this divergence persists as Kleinman has shown, which is also borne out by our analysis. The forms of the screening as a function of density, however, can be treated in some schemes which are discussed in Sec. V. The quantity of interest in the gradient expansion is Ω (in the notation of Sham[10]) as a function of density, and it is given in Fig. 1. For comparison, we have also plotted on the same graph those given by Sham and Kleinman. As shown in this paper, Sham's analysis is exact for high densities and is zero in this limit; we are in agreement with this result in contrast to Kleinman. For low densities, Kleinman's analysis is correct within the density-dependent screening model where Ω again approaches zero. Sham's procedure is inapplicable here, as his analysis was specially designed for high densities, as shown in Sec. V. These features are brought out explicitly in our analysis. Section V also contains details of these calculations. These various features are due to a proper combination of the renormalizations and

to the screening being a function of density in the form specified in Sec. V. Even more important, the antiparallel spin correlations are not taken into account in a linearized vertex equation, and only recently have we made progress in a variational solution to the nonlinear vertex equation.[14] We also present here a short summary of the results obtained.

II. SOLUTION OF THE IRREDUCIBLE VERTEX EQUATION

The longitudinal static dielectric function may be expressed in terms of the irreducible density-correlation function and the associated irreducible vertex function as

$$\epsilon_L(q) = 1 + (4\pi/q^2)\chi(q), \tag{1}$$

where

$$\chi(q) = 2e^2 \int \mathcal{F}(k, q)\Gamma(k;q)[d^3k/(2\pi)^3]. \tag{2}$$

Here $\mathcal{F}(k, q)$ is given by

$$\mathcal{F}(k, q) = -\frac{f_0(\vec{k} + \frac{1}{2}\vec{q}) - f_0(\vec{k} - \frac{1}{2}\vec{q})}{\epsilon_{\vec{k}+1/2\vec{q}} - \epsilon_{\vec{k}-1/2\vec{q}}}, \tag{3}$$

with ϵ_k the noninteracting one-electron energy, and $f_0(k)$ the Fermi function associated with the interacting electron of state $\vec{k}$. $\Gamma(k;q)$ obeys the linear integral equation in the random-phase approximation when the antiparallel spin correlations are neglected,[14]

$$\Gamma(k;q) = 1 + \int \mathcal{V}_s(|\vec{k} - \vec{k}_1|)\mathcal{F}(k_1, q)$$

$$\times \left[\Gamma(k_1;q) - \left(\frac{\epsilon_{\vec{k}_1+\vec{q}/2} - \epsilon_{\vec{k}_1-\vec{q}/2}}{\epsilon_{\vec{k}+\vec{q}/2} - \epsilon_{\vec{k}-\vec{q}/2}}\right)\Gamma(k;q)\right]\frac{d^3k_1}{(2\pi)^3} \tag{4}$$

This equation is the same one that Sham[10] and Kleinman[11] considered except that we have written it in such a way as to display in an explicit way the correlation contribution to the one-electron energy. It is for this reason we use the notation Γ instead of their $\bar{\Lambda}$. The advantages of doing this will become evident shortly. The interaction potential $\mathcal{V}_s(|\vec{k} - \vec{k}_1|)$ represents the statically screened electron-electron interaction. It is for this reason $\Gamma(k;q)$ does not depend on the frequency part associated with k. We shall not specify its form here.

We will now express these equations in dimensionless form, as is done in Ref. 1. Thus, in the notation of Ref. 1, we have

$$\chi(q) = \left(\frac{me^2 k_F}{2\pi^2}\right) \int x^{1/2} dx \int \frac{d\hat{x}}{4\pi} \mathcal{F}(x, y)\Gamma(x; y), \tag{5}$$

and

$$\Gamma(x; y) = 1 + \left(\frac{2\alpha r_s}{\pi}\right) \int x_1^{1/2} dx_1 \int \frac{d\hat{x}_1}{4\pi} V_s(|\vec{x} - \vec{x}_1|)$$

$$+\frac{1}{18}\frac{d^2}{dx_1^2}\left\{x_1^{3/2}\left[\Gamma_{00}^{(0)}(x_1)V_s^{(0)}(x;x_1)+\frac{4}{5}\left(\frac{x_1}{x}\right)^{1/2}\Gamma_{00}^{(0)}(x)\frac{V_s^{(3)}(x;x_1)}{7}-\frac{9}{5}\left(\frac{x_1}{x}\right)^{1/2}\Gamma_{00}^{(0)}(x)\frac{V_s^{(1)}(x;x_1)}{3}\right]\right\}\bigg)_{x_1=1}\delta_{l,0}\delta_{m,0}$$

$$+\frac{2\alpha r_s}{\pi}\left(\frac{1}{6}\frac{d^2}{dx_1^2}\left\{x_1^{3/2}\left[\frac{1}{3}\Gamma_{00}^{(0)}(x_1)\left(\frac{4}{5}\right)^{1/2}\frac{V_s^{(2)}(x;x_1)}{5}-\frac{1}{3}\left(\frac{x_1}{x}\right)^{1/2}\Gamma_{00}^{(0)}(x)\left(\frac{4}{5}\right)^{1/2}\frac{V_s^{(3)}(x;x_1)}{7}\right]\right\}\right)_{x_1=1}\delta_{l,2}\delta_{m,0}. \quad (15)$$

Once again, provided that Eq. (14) holds, we obtain an explicit solution for $\Gamma_{lm}^{(2)}(x)$ *which is nonzero only for* $l=0,2$ *and* $m=0$.

We now obtain for $\chi(q)$ the expression calculated to second order in q,

$$\chi(q)\cong\left(\frac{me^2k_F}{4\pi^3}\right)(4\pi)^{1/2}\left\{\Gamma_{00}^{(0)}(1)+y^2\left[\Gamma_{00}^{(2)}(1)-\frac{1}{4}\frac{d}{dx}[x^{1/2}\Gamma_{00}^{(0)}(x)]+\frac{1}{18}\frac{d^2}{dx^2}[x^{3/2}\Gamma_{00}^{(0)}(x)]+\frac{1}{18}\left(\frac{4}{5}\right)^{1/2}\frac{d^2}{dx^2}[x^{3/2}\Gamma_{20}^{(0)}(x)]\right]_{x=1}\right\}.$$

In view of the solutions obtained above, we finally express in the form

$$\chi(q)\cong\left(\frac{me^2k_F}{\pi^2}\right)\Gamma\left(1+\frac{y^2}{4}\left\{\left(-\frac{d}{dx}[x^{1/2}\bar{\Gamma}(x)]+\frac{2}{9}\frac{d^2}{dx^2}[x^{3/2}\bar{\Gamma}(x)]\right)_{x=1}+\left(\frac{2\alpha r_s}{\pi}\right)\Gamma\left[-\frac{d}{dx}\left(x^{1/2}\bar{\Gamma}(x)V_s^{(0)}(x;1)\right.\right.\right.\right.$$

$$\left.\left.\left.\left.-x\frac{V_s^{(1)}(x;1)}{3}\right)+\frac{2}{9}\frac{d^2}{dx^2}\left(x^{3/2}\bar{\Gamma}(x)V_s^{(0)}(x;1)+\frac{4}{5}x^2\frac{V_s^{(3)}(x;1)}{7}-\frac{9}{5}x^2\frac{V_s^{(1)}(x;1)}{3}\right)\right]_{x=1}\right\}\right). \quad (16)$$

This is the result of an exact solution to the irreducible equation, Eq. (6). In Sec. III, we will merely give the variational result calculated to the same order, and compare it with Eq. (16).

III. VARIATIONAL RESULT AND COMPARISON WITH OTHER RESULTS

In Ref. 3, the vertex equation, Eq. (6), is solved by a variational method, and $\chi(q)$ is computed for general wave vector q, frequency ω. In this, we set $\omega=0$ and compute the static expression up to q^2 order. Without giving the details of computation, we quote the final result here, in the present notation,

$$\chi_{var}(q)\cong\left(\frac{me^2k_F}{\pi^2}\right)\Gamma\left(1+\frac{y^2}{4}\left\{-\frac{2}{3}+\frac{1}{3}\Gamma+\left(\frac{2\alpha r_s}{\pi}\right)\Gamma\left[-\frac{d}{dx}\left(2x^{1/2}V_s^{(0)}(x;1)-(x+1)\frac{V_s^{(1)}(x;1)}{3}\right)\right.\right.\right.$$

$$\left.\left.\left.+\frac{2}{9}\frac{d^2}{dx^2}\left(2x^{3/2}V_s^{(0)}(x;1)-\frac{9}{5}x^2\frac{V_s^{(1)}(x;1)}{3}-x\frac{V_s^{(1)}(x;1)}{3}+\frac{4}{5}x^2\frac{V_s^{(3)}(x;1)}{7}\right)\right]_{x=1}\right\}\right), \quad (17)$$

It may be of interest to point out that the variational solution to the vertex equation has the structure

$$\Gamma_{var}(x;y)=I(y)/[I(y)-J(y)], \quad (18)$$

where

$$I(y)=\int x^{1/2}dx\int d\hat{x}\,\mathcal{F}(x;y) \quad (18a)$$

and

$$J(y)=(\alpha r_s/2\pi^2)\int x^{1/2}dx\int d\hat{x}\int x_1^{1/2}dx_1\int d\hat{x}_1$$

$$\times\mathcal{F}(x,y)\mathcal{F}(x_1,y)V_s(|\vec{x}-\vec{x}_1|)$$

$$\times[1-(x_1/x)^{1/2}\cos\theta_{x_1}/\cos\theta_x]. \quad (18b)$$

Observe that the trial solution $\Gamma_{var}(x;y)$ has no x dependence at all. When we compare Eqs. (16) and (17), we will be surprised to find that the difference between them has a simple form:

$$\chi(q)=\chi_{var}(q)+y^2\left(\frac{me^2k_F}{\pi^2}\right)\frac{1}{9}\Gamma^2\left(\frac{2\alpha r_s}{\pi}\right)^2 Z_1$$

$$\times\left[\frac{d}{dx}\left(V_s^{(0)}(x;1)-x^{-1/2}\frac{V_s^{(1)}(x;1)}{3}\right)\right]_{x=1}^2. \quad (19)$$

Here

$$Z_1=1/[1+(2\alpha r_s/\pi)\tfrac{1}{3}V_s^{(1)}(1;1)]. \quad (20)$$

In deriving Eq. (19), one makes use of many simplifying properties that $\bar{\Gamma}(x)$ enjoys, even though the actual computation is somewhat tedious.

In Sec. IV, we will discuss in detail the various aspects of a very popular model for $V_s(|\vec{x}-\vec{x}_1|)$, namely the Yukawa potential.

IV. COMPUTATION OF $g_{xc}^{(2)}$ OF THE GRADIENT EXPANSION

Sham[10] has shown that if one writes $\chi(q)$ in the form (we use the notations as in Sham's paper)

$$\chi(q)\cong\chi^{(0)}+q^2\chi^{(2)}, \quad (21)$$

then the coefficient $g_{xc}^{(2)}(n)$ of the gradient expansion in the theory of the inhomogeneous electron system is

$$g_{xc}^{(2)}(n)=[\chi^{(2)}/(\chi^{(0)})^2-\chi_0^{(2)}/(\chi_0^{(0)})^2], \quad (22)$$

where the subscripts 0 indicate the same quantities for the noninteracting system with the same density.

If $E_{xc}[n]$ is the exchange and correlation energy functional, Kleinman defined[11]

$$E_{xc}[n] = \int \epsilon_{xc}(n) n \, d^3r + \tfrac{1}{2} \int g_{xc}^{(2)}(n) |\vec{\nabla} n|^2 \, d^3r + \cdots ,$$

where $\epsilon_{xc}(n)$ is the exchange and correlation energy per electron in the uniform gas. This serves to define $g_{xc}^{(2)}$. The latter are easily calculated because in the expressions for $\chi^{(0)}$, $\chi^{(2)}$, if we set the terms containing $V_s^{(1)}$ zero, we obtain $\chi_0^{(0)}$, $\chi_0^{(2)}$, respectively.

We first make the observation that if we employ the first iterative solution to the $\Gamma(x;y)$ equation as was done by Sham,[10] we obtain

$$\Gamma(x;y) \cong 1 + \left(\frac{\alpha r_s}{2\pi} \right) \int x_1^{1/2} dx_1 \int d\hat{x}_1 V_s(|\vec{x} - \vec{x}_1|)$$
$$\times \mathcal{F}(x_1;y) \left[1 - \left(\frac{x_1}{x} \right)^{1/2} \frac{\cos\theta_{x_1}}{\cos\theta_x} \right]. \qquad (23)$$

Using this in Eq. (5) and the notations (18a, 18b), we obtain

$$\chi_{Sham}(q) \cong (m k_F e^2 / 4\pi^3) [I(y) + J(y)]. \qquad (24)$$

Even though the variational solution is of the form (18), in contrast to the iterative solution (23), we observe that $\chi_{var}(q)$ is found to be

$$\chi_{var}(q) = \left(\frac{m k_F e^2}{4\pi^3} \right) \frac{[I(y)]^2}{I(y) - J(y)} . \qquad (25)$$

Sham's procedure is equivalent to expanding $\chi(q)$ up to first order in $\alpha r_s / \pi$, and so expanding $\chi_{var}(q)$ up to this order. We observe this to be the *same expression* as Sham's.

On the other hand, if we use $\chi_{var}(q)$ to compute it to order q^2, we obtain

$$\chi_{var}(q) \cong \left(\frac{m k_F e^2}{4\pi^3} \right) \Gamma I^{(0)} \left\{ 1 + \left[2\frac{I^{(2)}}{I^{(0)}} - \Gamma\left(\frac{I^{(2)}}{I^{(0)}} - \frac{J^{(2)}}{I^{(0)}} \right) \right] y^2 \right\},$$
$$\qquad (26)$$

and Sham obtains

$$\chi_{Sham}(q) \cong \left(\frac{m k_F e^2}{4\pi^3} \right) I^{(0)} \left[1 + \frac{J^{(0)}}{I^{(0)}} + \left(\frac{I^{(2)}}{I^{(0)}} + \frac{J^{(2)}}{I^{(0)}} \right) y^2 \right]. \qquad (27)$$

This essentially means that the vertex renormalization $\Gamma [\equiv (1 - J^{(0)}/I^{(0)})^{-1}]$ is set equal to $1 + J^{(0)}/I^{(0)}$ in Sham's procedure. Since setting $J = 0$ and $\Gamma = 1$ imply that we are dealing with the noninteracting system, we obtain for $g_{xc}^{(2)}$ the following expressions (in our notation):

$$g_{xc}^{(2)}(var) = 4\pi^3 / m k_F e^2 I^{(0)} \Gamma$$
$$\times \{ 2(I^{(2)}/I^{(0)})[(1-\Gamma)/\Gamma] + J^{(2)}/I^{(0)} \}, \qquad (28a)$$

and

$$g_{xc}^{(2)}(exact) = \frac{4\pi^3}{m k_F e^2 I^{(0)} \Gamma} \left\{ 2\frac{I^{(2)}}{I^{(0)}}\left(\frac{1-\Gamma}{\Gamma}\right) + \frac{J^{(2)}}{I^{(0)}} + \left(\frac{2\alpha r_s}{\pi}\right)^2 Z_1 \left[\frac{d}{dx}\left(V_s^{(0)}(1;x) - x^{-1/2}\frac{V_s^{(1)}(1;x)}{3} \right) \right]_{x=1}^2 \right\}$$

$$\equiv g_{xc}^{(2)}(var) + \frac{4\pi^3}{m k_F e^2 I^{(0)} \Gamma} \left(\frac{2\alpha r_s}{\pi} \right)^2 Z_1 \left[\frac{d}{dx}\left(V_s^{(0)}(1;x) - x^{-1/2}\frac{V_s^{(1)}(1;x)}{3} \right) \right]_{x=1}^2 . \qquad (28b)$$

Now from Eq. (17), we may deduce

$$I^{(0)} = 4\pi, \quad I^{(2)}/I^{(0)} = -\tfrac{1}{12},$$

$$\Gamma = \left[1 - \left(\frac{2\alpha r_s}{\pi} \right)[V_s^{(0)}(1;1) - \tfrac{1}{3}V_s^{(1)}(1;1)] \right]^{-1},$$

and

$$\frac{J^{(2)}}{I^{(0)}} = \left(\frac{2\alpha r_s}{\pi} \right) \left[-\frac{1}{4}\frac{d}{dx}\left(2x^{1/2} V_s^{(0)}(1;x) - (1+x)\frac{V_s^{(1)}(1;x)}{3} \right) + \frac{1}{18}\frac{d^2}{dx^2}\left(2x^{3/2} V_s^{(0)}(1;x) - \frac{9}{5}x^2\frac{V_s^{(1)}(1;x)}{3} \right. \right.$$

$$\left. \left. + \frac{4}{5}x^2\frac{V_s^{(3)}(1;x)}{7} - x\frac{V_s^{(1)}(1;x)}{3} \right) \right]_{x=1} . \qquad (29)$$

Thus we see that the variational result is obtained when Z_1 is set equal to zero, and Sham's answer is obtained when Z_1 is set equal to zero, and Γ equal to $1 + J^{(0)}/I^{(0)}$, and working to first power in $\alpha r_s/\pi$ (high-density limit) in the exact expressions. The correction to the variational answer is thus seen to be of order $(\alpha r_s/\pi)^2$ including powers of $\alpha r_s/\pi$ in Eq. (28b) without those appearing in Γ and Z_1, as they are of magnitude unity plus corrections of order $\alpha r_s/\pi$ provided that the expressions multiplying them are finite in this limit. In Sec. V, we will specialize the above results in terms of a Yukawa form for $V_s(|\vec{k} - \vec{k}_1|)$ and discuss the expressions in various regions of validity of such a model. We may state here that by expressing our results in terms of $V_s^{(1)}$ as above, we

have made a contact with Fermi-liquid-theory parameters, which are being experimentally measured these days.

V. YUKAWA INTERACTION MODEL AND DISCUSSION OF THE RESULTS

We will consider the effective interaction potential between the electrons to be of the Yukawa form, which enables us to perform all the calculations explicitly in terms of one parameter, the screening parameter.[1] Thus,

$$V_s(|\bar{x} - \bar{x}_1|) = 1/[x + x_1 - 2(xx_1)^{1/2}\cos\theta_{xx_1} + \xi^2],$$

(30)

and so,

$$\frac{V_s^{(1)}(x; x_1)}{2l+1} = \frac{1}{2(xx_1)^{1/2}} \, Q_l\left(\frac{x + x_1 + \xi^2}{2(xx_1)^{1/2}}\right),$$

(31)

where Q_l is the usual associated Legendre function. We then obtain

$$\Gamma = 1\left/\left\{1 - \frac{\alpha r_s}{\pi}\left[1 - \frac{\xi^2}{4}\ln\left(1 + \frac{4}{\xi^2}\right)\right]\right\}\right. ;$$

$$Z_1 = 1\left/\left\{1 + \frac{\alpha r_s}{\pi}\left[\frac{1}{2}\left(1 + \frac{\xi^2}{2}\right)\ln\left(1 + \frac{4}{\xi^2}\right) - 1\right]\right\}\right. ,$$

(32)

$$\frac{J^{(2)}}{I^{(0)}} = \frac{1}{72}\left(\frac{\alpha r_s}{\pi}\right)\left[6 - \frac{36}{\xi^2+4} - \frac{32}{(\xi^2+4)^2} - \tfrac{3}{2}\xi^2\ln\left(1 + \frac{4}{\xi^2}\right)\right],$$

(33)

and

$$\left[\frac{d}{dx}\left(V_s^{(0)}(1; x) - x^{-1/2}\frac{V_s^{(1)}(1; x)}{3}\right)\right]_{x=1}$$

$$= \frac{1}{2}\left[-1 - \frac{\xi^2}{2(4+\xi^2)} + \left(\frac{1}{4} + \frac{3\xi^2}{8}\right)\ln\left(1 + \frac{4}{\xi^2}\right)\right].$$

(34)

Several features of this model may be of value and so we record them here:

(i) In the large ξ limit (i.e., short-range model), the vertex equation can be solved exactly and one has to observe that the coupling strength is now $\alpha r_s/\pi\xi^2$ which is held constant. In this limit, we have $Z_1 = 1$, but $[d(V_s^{(0)} - \frac{1}{3}x^{-1/2}V_s^{(1)})/dx]_{x=1} \simeq O(1/\xi^4)$, and so the variational result coincides *completely with the exact answer*, as is to be expected.

(ii) In the limit of Coulomb interactions, i.e., $\xi \to 0$, we observe that Z_1 goes to zero like

$$1\left/\left[\left(\frac{\alpha r_s}{2\pi}\right)\ln(4/\xi^2)\right]\right. ;$$

$$\left(\frac{2\alpha r_s}{\pi}\right)^2\left[\frac{d}{dx}(V_s^{(0)} - x^{-1/2}V_s^{(1)}/3)\right]_{x=1}^2$$

diverges like $(\alpha r_s/2\pi)^2[\ln(4/\xi^2)]^2$ so that the correction to the variational answer diverges like $(\alpha r_s/2\pi)\ln(4/\xi^2)$. *In the strictly Coulomb limit, one has therefore a divergence* for a fixed r_s (or

k_F). A similar result is also obtained by Kleinman.[11] But Kleinman takes ξ^2 to be the Thomas-Fermi expression, i.e., $\xi^2 \, 4\alpha r_s/\pi$ and claims that now there is no divergence, as $r_s \to 0$. Hence, as long as ξ is treated as an independent parameter not depending on the electron density, one has a divergence, while if it depends on r_s, this divergence disappears. Now $\xi \to 0$ implies in the Thomas-Fermi model for screening that $r_s \to 0$; and so, the only inference possible is that in the high-density limit, the corrections to the variational answer are again zero. Also, we may point out that Sham's result is not expected to be correct for low densities, where $r_s \to \infty$ (or $k_F \to 0$).

(iii) In Ref. 13, we have developed a self-consistent scheme to determine ξ^2. The argument runs as follows. We know that in the limit of zero q, $q^2\epsilon_L(q)$ gives ξ^2. We have computed $\epsilon_L(q)$ using a Yukawa interaction, and this new expression for it should be consistent with the above general result. Thus, we obtain[13]

$$\xi_{sc}^2 = (4\pi/k_F^2)\lim_{q\to 0}\chi(q) \, (4\pi/k_F^2)\chi^{(0)},$$

or

$$\xi_{sc}^2 = \frac{4\alpha r_s}{\pi}\Gamma\left(\frac{4\alpha r_s}{\pi}\right)\left/\left\{1 - \left(\frac{\alpha r_s}{\pi}\right)\right.\right.$$
$$\left.\left.\times\left[1 - \tfrac{1}{4}\xi_{sc}^2\ln\left(1 + \frac{4}{\xi_{sc}^2}\right)\right]\right\}\right. .$$

(35)

This may be rewritten in the form

$$\frac{\alpha r_s}{\pi} = (\tfrac{1}{4}\xi_{sc}^2/[1 + \tfrac{1}{4}\xi_{sc}^2 - \tfrac{1}{16}\xi_{sc}^4\ln(1 + 4/\xi_{sc}^2)].$$

(36)

This equation can be solved graphically to determine ξ_{sc}^2 as a function of $\alpha r_s/\pi$. We observe that $\xi_{sc}^2 \to 0$ only if $\alpha r_s/\pi \to 0$, i.e., only in the very high-density limit. Thus the Thomas-Fermi relationship is reliable only for very high density of the electron gas. Also, for $\xi^2 \to \infty$, we observe the right-hand side of Eq. (36) becomes proportional to $\frac{2}{3}(\xi_{sc}^2/4)$. Thus in the low-density limit, the screening, though similar to the Thomas-Fermi expression, is different by a factor $\frac{1}{3}$. This is not a reliable answer since one expects for very low densities zero screening.

It is worth noting that $\Omega(k_F) - (k_F^3/\pi^2)g_{sc}^{(2)}$, calculated using our formalism, vanishes in the two extreme limits of $\pi k_F \to 0$ (low density) and $\pi k_F \to \infty$ (high density) in contrast with the result of Kleinman.[11] Kleinman obtained a constant value for $\Omega(k_F)$ for $\pi k_F \to \infty$ (high density). To check if this would obtain in our formalism too, if we took ξ^2 to be the Thomas-Fermi value $4\alpha r_s/\pi$, we made a similar asymptotic calculation from our expression for $\Omega(k_F)$, and we found this to vanish. For $\pi k_F \to \infty$, we have the extreme high-density limit where Sham's procedure[10] is certainly valid, as is

lso evident from our analysis.
$(k_F) - 0$ for $\pi k_F \to \infty$, and we are in agreement with
im. For $\pi k_F \to 0$ (low density), we agree with
leinman's result that $\Omega \to 0$ again, whereas Sham's
esult is divergent but inappropriate in this limit.
1 view of the various comments made on the
ukawa model, it appears a calculation of $\Omega(k_F)$
ith a more realistic momentum-dependent inter-
:tion potential should be made. In Fig. 1 we have
isplayed our results. It is found that the variation-
l results are in excellent agreement with the exact
esults for both high and low densities, except the
osition and height of the maximum are slightly
ifferent. We have therefore displayed only the
:act results for the self-consistent and Thomas-
ermi schemes for ξ^8. The other contrasting fea-
ires with the results of Sham and Kleinman are
vident from this figure. A numerical table of Ω
3 πk_F may be obtained on request, from either
: the authors.

Professor Kleinman has informed one of us
(A.K.R.) that he has now verified that his Ω also
vanishes for $\pi k_F \to \infty$, in agreement with Sham and
our result. The general shape of his curve of Ω
vs πk_F now is the same as ours but seems to have
some *small* differences in detail. We thank Pro-
fessor Kleinman for informing us of his new finding
and for pointing out a sign error in the definition
of Ω in terms of $g_{\bar{m}}^{(2)}$. We must mention that we have
also come across a paper by Geldart *et al.* [Solid
State Commun. 16, 243 (1975)], where a rigorous
analysis of the $g_{\bar{m}}^{(2)}$ is also made, and their con-
clusions in certain limits seem to be in general
agreement with ours. These authors do not give
a graph of Ω vs πk_F.

ACKNOWLEDGMENT

Jn leave from and address after August 1, 1975, De-
partment of Physics and Astronomy, Louisiana State
University, Baton Rouge, La. 70803.

. K. Rajagopal, Phys. Rev. 142, 152 (1966).

. K. Rajagopal and K. P. Jain, Phys. Rev. A 5, 1475
1972).

. K. Rajagopal, Phys. Rev. A 6, 1239 (1972).

. K. Rajagopal, J. Rath, and J. Kimball, Phys. Rev.
3 7, 2657 (1973).

. K. Rajagopal and G. S. Grest, Phys. Rev. B 9, 268
1974).

'. Hohenberg and W. Kohn, Phys. Rev. 136, B 864
(1964).

V. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

I. D. Lang has reviewed the density-functional formal-
ism and its application to surface problems in *Advances
in Solid State Physics*, edited by H. Ehrenreich, F.
Seitz, and D. Turnbull (Academic, New York, 1973),
Vol. 28, p. 225.

[9]A. K. Rajagopal and J. Callaway, Phys. Rev. B 7, 1912
(1973), the density-functional formalism is generalized
to include current densities and, thus, also an inhomo-
geneous magnetic system. M. M. Pant and A. K. Raja-
gopal [Solid State Commun. 10, 1157 (1972)] applied
this to the problem of the work function of a ferromag-
netic surface.

[10]L. J. Sham, in *Computational Methods in Band Theory*,
edited by P. J. Marcus, J. F. Janak, and A. R. Wil-
liams (Plenum, New York, 1971), p. 458.

[11]L. Kleinman, Phys. Rev. B 10, 2221 (1974). We thank
Professor Kleinman for sending us a preprint of this
paper before its publication.

[12]A. K. Rajagopal, Pramāṇa 4, 140 (1975).

[13]B. Sriram Shastry, Sudhanshu S. Jha, and A. K. Raja-
gopal, Phys. Rev. B 9, 2000 (1974).

[14]A. R. P. Rau and A. K. Rajagopal, Solid State Commun.
16, 1027 (1975). A fuller version of this work has now
appeared in Phys. Rev. B 11, 3604 (1975).